# RUBBER CHEMISTRY

# AND TECHNOLOGY

# Non-Staining Antioxidants for White or Light-Colored Rubber

Applied to antioxidants for use in rubber products, the term "non-staining" describes those materials which: (a) themselves impart no color to the rubber product; (b) develop no color and produce no color change in the rubber product or on its surface when exposed to light or other aging conditions; and (c) impart no discoloration by transfer-staining to adjoining light-colored surfaces.

Even in the absence of an antioxidant, white or light-colored rubber products may show some discoloration or color change when exposed to light and aging. The problem, then, is the development of antioxidants which will greatly improve aging qualities and service life without accentuating this natural color change. Antioxidants which fulfill this condition may justly be called "non-staining" antioxidants.

The best non-staining antioxidants belong to the class of chemicals known as phenols. This class of antioxidants seems to be expanding, and several new products have been added in recent years. They are not uniformly good, however, for phenolic-type chemicals vary in their antioxidant activity from "slight" to "very good"; they also vary in the degree of discoloration produced in the rubber. The ideal is, of course, an antioxidant which is highly effective in extending the storage or service life of the rubber product while causing no discoloration or color change whatsoever. While this ideal balance has not yet been achieved, several phenolic antioxidants give performances closely approaching it.

In a test designed to show their relative effectiveness, six typical phenolic-type antioxidants were examined against Cyanamid's Antioxidant 2246® and Antioxidant 425®.

**Product A** (in ratios of 0.5 to 1.0 %/RHC) gave only fair protection against normal aging, together with slight discoloration on exposure to sunlight.

**Product B** (in ratios of 0.25 to 1.0%) gave moderate protection against oxidation, flexing and frosting, with a small amount of discoloration on exposure to sunlight.

**Product C** (in ratios of 1.0 to 2.0%) gave practically no discoloration, but only mild protection against oxidation.

**Product D** (in ratios of 1.0 to 2.0%) also gave practically no discoloration, but only mild protection against oxidation.

**Product E** (in ratios of 1.0 to 2.0%) gave very good protection against oxidation, but with a small amount of discoloration on exposure to sunlight.

**Product F** (in ratios of 1.0 to 2.0%) also gave very good protection against oxidation, with very slight discoloration on exposure to sunlight.

**Antioxidant 2246** (in ratios of 0.25 to 2.0%) gave very good protection against oxidation, proved beneficial against flexing and surface oxidation induced by light, and produced only a slight amount of discoloration in white rubber on exposure to sunlight.

**Antioxidant 425** (in ratios of 0.25 to 2.0%) gave very good protection against oxidation, with practically no discoloration in white rubber on exposure to sunlight.

Conditions were identical for all eight antioxidants examined. The results proved that, for white or light-colored products made from dry rubber or latex, Cyanamid's Antioxidant 2246 and Antioxidant 425 offer the best combined protection against aging and discoloration.

These two great antioxidants were developed as a result of lengthy research work in Cyanamid's laboratories. However, the only real test of a product's worth is its actual field performance. In this respect, Antioxidant 2246 and Antioxidant 425 have fully proved their claims of being the finest available anywhere.

For full technical information, write for Rubber Chemicals Technical Bulletins No. 815 (Antioxidant 2246) and No. 840 (Antioxidant 425).

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# RUBBER CHEMISTRY AND TECHNOLOGY

# THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

## OFFICERS AND EXECUTIVE COMMITTEE

## COMMITTEES

*Education*....C. V. LUNDBERG, *Chairman* (Bell Telephone Laboratories), R. G. SEAMAN (*Rubber World*), M. L. STUDEBAKER (Phillips Chemical Co.), R. D. STIEHLER (National Bureau of Standards), W. F. BUSSE (E. I. du Pont de Nemours & Co.).

*Files and Records*....J. D. D'IANNI, *Chairman* (Goodyear Tire & Rubber Co.), DOROTHY HAMLEN (University of Akron), E. A. WILLSON (B. F. Goodrich Research Center).

*Future Meetings*....A. E. LAURENCE, *Chairman* (Phillips Chemical Co.), G. N. VACCA (Bell Telephone Laboratories), E. B. BUSENBERG (The B. F. Goodrich Co.).

*Library Policy Committee*....RALPH F. WOLF, *Chairman* (Columbia-Southern Chemical Corp.), B. S. GARVEY, JR. (Penn. Salt Mfg. Co.), O. D. COLE (Firestone Tire & Rubber Co.), N. V. SEEGER (Diamond Alkali Co.), G. E. POPP *Ex-officio* (Phillips Chemical Co.).

*Library Operating Committee*....LOIS BROCK, *Chairman* (General Tire & Rubber Co.), FERN BLOOM (B. F. Goodrich Research Center), LILLIAN COOK (University of Akron), DOROTHY HAMLEN (University of Akron), ANNE HILDEBRAND (Firestone Tire & Rubber Co.).

*Membership*....H. W. HOERAUF, *Chairman* (United States Rubber Co.), with members from each Local Rubber Group.

*Nominating*....D. F. BEHNEY, *Chairman* (Harwick-Standard Chemical Co.), H. G. BIMMERMAN (E. I. du Pont de Nemours & Co.), R. A. EMMETT (Columbian Carbon Co.), L. M. FREEMAN (The B. F. Goodrich Co.), H. J. OSTERHOF (Goodyear Tire & Rubber Co.).

*Papers Review*....B. S. GARVEY, JR. (Penn. Salt Mfg. Co.), C. C. DAVIS, 7 Ravine Road, Winchester, Mass., A. M. NEAL (E. I. du Pont de Nemours & Co.), A. E. JUVE (The B. F. Goodrich Research Center), R. F. DUNBROOK (Firestone Tire & Rubber Co.), D. CRAIG (B. F. Goodrich Research Center), N. S. GRACE (Dunlop Research Center).

*New Publications*....N. BEKKEDAHL, *Chairman* (National Bureau of Standards), R. G. SEAMAN (*Rubber World*), D. CRAIG (B. F. Goodrich Research Center).

*Tellers*....R. A. GARRETT, *Chairman* (Armstrong Cork Co.), S. R. SHUART (Enjay Laboratories), D. B. FORMAN (E. I. du Pont de Nemours & Co.).

*Nomenclature*....R. G. SEAMAN, *Chairman* (*Rubber World*), I. D. PATTERSON (Goodyear Tire & Rubber Co.), F. W. GAGE (Dayton Chemical Products Laboratories), E. E. GRUBER (General Tire & Rubber Co.), ROY M. VANCE (Columbian Carbon Co.).

*Finance and Budget*....L. V. COOPER, *Chairman* (Firestone Tire & Rubber Co.), S. B. KUYKENDALL (Firestone Tire & Rubber Co.), E. H. KRISMANN (E. I. du Pont de Nemours & Co.), G. E. POPP *Ex-officio* (Phillips Chemical Co.).

*By-Laws Revision*....W. L. SEMON, *Chairman* (B. F. Goodrich Research Center), GLEN ALLIGER (Firestone Research), D. F. REAHARD JR. (Wabash Rubber and Plastics Corp.).

*Best Paper*....W. R. SMITH, *Chairman* (Godfrey L. Cabot), E. B. NEWTON (B. F. Goodrich Research Center).

*Officers Manual*....S. G. BYAM, *Chairman* (E. I. du Pont de Nemours & Co.), J. M. BALL (Midwest Rubber Reclaiming Co.).

*Office of Permanent Historian*....H. L. TRUMBULL

## FUTURE MEETINGS

| Meeting | | City | Hotel | Date |
|---|---|---|---|---|
| 1957 | Fall | New York | Commodore | September 11–13 |
| 1958 | Spring | Cincinnati | Netherlands Plaza | May 14–16 |
| 1958 | Fall | Chicago | Sherman | September 10–12 |
| 1959 | Spring | Los Angeles | Biltmore | May 12–15 |
| 1959 | Fall | Washington* | Shoreham | November 9–13 |
| 1960 | Spring | Buffalo | Statler | May 24–27 |
| 1960 | Fall | New York | Commodore | September 13–16 |
| 1961 | Spring | Louisville | Brown | May 16–19 |
| 1961 | Fall | Chicago | Sherman | September 5–8 |
| 1962 | Spring | Boston | Statler | May 15–18 |

* An international meeting jointly sponsored by the Division of Rubber Chemistry ACS, Committee D-11 of ASTM, and the Rubber and Plastics Division of ASME.

## SPONSORED RUBBER GROUPS

## OFFICERS AND MEETING DATES

### 1957

#### AKRON

*Chairman:* Sheldon Nicol (Goodyear Tire and Rubber Co., Akron). *Asst. to Chairman* K. R. Garvick (Mansfield Tire and Rubber Co., Mansfield). *Secretary:* Milton H. Leonard (Columbian Carbon Co., Akron). *Treasurer:* George Popp (Phillips Chemical Company, Akron). Terms end June 30, 1958. Meetings in 1957: October 25; in 1958: January 24, April 11, and June 20.

#### BOSTON

*Chairman:* Arthur I. Ross (American Biltrite Rubber Co., Chelsea). *Vice-Chairman:* Roger Steller (B. F. Goodrich Chemical Co., Boston). *Secretary-Treasurer:* William King (Acushnet Process Co., New Bedford). Terms end December 31, 1957. Meetings in 1957: March 15, June 14, October 18, December 13.

#### BUFFALO

*Chairman:* Charles Miserentino (Dunlop Tire & Rubber Co., Buffalo). *Vice-Chairman:* John Helwic (Dunlop Tire & Rubber Co., Buffalo). *Secretary-Treasurer:* Richard Herdlein (Hewitt-Robins, Inc., Buffalo). Terms end December 31, 1957. Meetings in 1957: March 5, May 10, June 11, October 8, December 3.

## CHICAGO

*Chairman:* A. E. Laurence (Phillips Chemical Co., Elmhurst). *Vice-Chairman:* V. Labrecque (Victor Mfg. & Gasket Co., Chicago). *Secretary:* M. J. O'Connor (O'Connor & Co., Inc., Chicago). *Treasurer:* J. Groot (Dryden Rubber Div., Sheller Mfg. Corp., Chicago). Terms end August 30, 1957. Meetings in 1957: October 20, November 15, December 20; in 1958: January 31, March 14 and April 25.

## CONNECTICUT

*Chairman:* Harry Gordon (Bond Rubber Corp., Derby). *Vice-Chairman:* R. T. Zimmerman (R. T. Vanderbilt Co., East Norwalk). *Secretary:* Vincent Chadwick (Armstrong Rubber Co., West Haven). *Treasurer:* William Couch (Whitney Blake Co., Hamden). Terms end January 1, 1958. Meetings in 1957: February 15, May 24, September 7, November 15.

## DETROIT

*Chairman:* H. F. Jacober (Baldwin Rubber Co., Pontiac). *Vice-Chairman:* E. J. Kvet, Jr. (Detroit Arsenal, Centerline). *Secretary:* S. R. Schaffer (U. S. Rubber Co., Detroit). *Treasurer:* W. F. Miller (Yale Rubber Mfg. Co., Detroit). Terms end December 31, 1957. Meetings in 1957: February 1, April 12, June 28, October 4, December 6.

## FORT WAYNE

*Chairman:* Maurice J. O'Connor (O'Connor & Co., Inc., Chicago). *Vice-Chairman:* George E. Kelsheimer (U. S. Rubber Co., Fort Wayne). *Secretary-Treasurer:* Philip Magner, Jr. (General Tire & Rubber Co., Wabash, Ind.). Terms end June 8, 1957. Meetings in 1957: February 7, April 11, June 7, September 26, December 5.

## LOS ANGELES

*Chairman:* Roy N. Phelan (Atlas Sponge Rubber Co., Monrovia). *Assoc. Chairman:* Albert H. Federico (C. P. Hall Co., Los Angeles). *Vice-Chairman:* Charles H. Kuhn (Master Processing Corp., Lynwood). *Secretary:* B. R. Snyder (R. T. Vanderbilt Co., Los Angeles). *Treasurer:* Ray E. Bitter (B. F. Goodrich Chemical Co., Los Angeles). Terms end December 31, 1957. Meetings in 1957: February 5, March 5, April 2, May 7, June 7, 8 and 9, October 1, November 5, December 13.

## NEW YORK

*Chairman:* Herbert J. Due (St. Joseph Lead Co., New York). *Vice-Chairman:* C. V. Lundberg (Bell Telephone Laboratories, Murray Hill, N. J.). *Secretary-Treasurer:* R. G. Seaman (*Rubber World*, New York). Terms end December 31, 1957. Meetings in 1957: March 22, October 4, December 13.

## NORTHERN CALIFORNIA

*Chairman:* Ralph T. Hickcox (Goodyear Tire & Rubber Co., San Francisco). *Vice-Chairman:* William H. Deis (Merck & Co., Inc., S. San Francisco).

*Secretary:* Keith Large (Oliver Tire & Rubber Co., Oakland). *Treasurer:* A. E. Barrett (Mare Island Naval Shipyard, Rubber Laboratory, Vallejo). Terms end December 31, 1957. Meetings in 1957: January 10, February 14, March 14, April 11, May 9, June 13, September 12, October 10, November 14, December 6.

## PHILADELPHIA

*Chairman:* J. R. Mills (Goodall Rubber Co., Trenton). *Vice-Chairman:* R. A. Garrett (Armstrong Cork Co., Lancaster). *Secretary-Treasurer:* R. S. Graff (E. I. du Pont de Nemours & Co., Trenton). Terms end January 25, 1958. Meetings in 1957: January 25, April 12, August, October 25, November.

## RHODE ISLAND

*Chairman:* G. E. Enser (Collyer Wire Co., Pawtucket). *Vice-Chairman:* W. K. Priestley (Kaiser Aluminum Corp., Bristol). *Secretary-Treasurer:* H. W. Day (E. I. du Pont de Nemours & Co., Boston). Terms end November, 1957. Meetings in 1957: April 4, June 6, November 7.

## SOUTHERN OHIO

*Chairman:* E. N. Cunningham (Precision Rubber Products Corp., Dayton). *Vice-Chairman:* Earle Bartholomew (Wright Patterson Air Force Base, Dayton). *Secretary:* R. J. Hoskin (Inland Mfg. Div., G. M. Corp., Dayton). *Treasurer:* H. F. Schweller (Inland Mfg. Div., G. M. Corp., Dayton). Terms end December 31, 1957. Meetings in 1957: March 28, June 1, October 24, December 14.

## WASHINGTON, D. C.

*Chairman:* D. K. Bonn (U. S. Rubber Co., Washington, D. C.). *Vice-Chairman:* R. D. Stiehler (National Bureau of Standards, Washington, D. C.). *Secretary:* A. W. Sloan (812 N. Fairfax St., Alexandria, Va.). *Treasurer:* J. Royden Moore (Firestone Tire and Rubber Co., Washington, D. C.). Terms end October, 1957. Meetings in 1957: January 16, February 13, March 20, April 17, May 15.

# PROVISIONAL NON-SPONSORED RUBBER GROUP

## SOUTHERN

### *Formed 1956, Provisional to 1958*

*Chairman:* John M. Bolt (Naugatuck Chemical Div., Olive Branch, Miss.). *Vice-Chairman:* T. R. Brown (B. F. Goodrich Co., Tuscaloosa, Ala.). *Secretary:* Roger B. Pfau (C. P. Hall Co., Memphis, Tenn.). *Treasurer:* Elden H. Ruch (Firestone Tire and Rubber Co., Memphis, Tenn.). Terms end October 31, 1957. Meetings in 1957: February 8 and 9, June 7 and 8, November 15 and 16.

# SECRETARIES OF RUBBER GROUPS

## AKRON

Mr. Milton H. Leonard
Columbian Carbon Co.
Akron, Ohio

## BOSTON

Mr. William King
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New Bedford, Massachusetts

## BUFFALO

Mr. Richard Herdlein, Jr.
Hewitt-Robins, Incorporated
240 Kensington Avenue
Buffalo 5, New York

## CHICAGO

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Room 417
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333 N. Michigan Ave.
Chicago 1, Illinois

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West Haven 16, Conn.

## DETROIT

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## FORT WAYNE

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Wabash, Indiana

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Trenton, New Jersey

## RHODE ISLAND

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18 Downing Street
Hingham, Massachusetts

## SOUTHERN OHIO

Mr. R. J. Hoskin
Inland Manufacturing Division
General Motors Corporation
2727 Inland Avenue
Dayton 7, Ohio

## WASHINGTON, D. C.

Mr. Robert D. Stiehler
National Bureau of Standards
Washington 25, D. C.

## PROVISIONAL NON–SPONSORED RUBBER GROUP

## SOUTHERN

Mr. Roger B. Pfau
C. P. Hall Company
648 Riverside Drive
Memphis 2, Tennessee

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# NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY, Vol. XX, 1956. Edited by T. J. Drakeley. Published by W. Heffer & Sons, Ltd., Cambridge, England, for the Institution of the Rubber Industry, 4 Kensington Palace Gardens, London, W. 8, England. Cloth cover, $7\frac{1}{4} \times 9\frac{3}{4}$ inches, 161 pages. Price $3.50.—This annual report of the IRI, as emphasized in the foreword, is exactly as defined by the title and is not a complete bibliography and should not be used as such. It is prepared to show the pattern or progress in rubber technology by use of selected items from the literature. However, the literature references are extensive and a name and a subject index are provided. The various chapters are prepared by leading authorities in their fields and include a historical and statistical review; planting and production of raw rubber and latex; properties, applications, and utilization of latex; chemistry of raw and vulcanized rubber; physics of raw and vulcanized rubber, synthetic rubber, testing and equipment and specifications; and compounding ingredients. Observations made of the progress in the fields of belting, footwear, mechanical rubber goods, and cellular rubber are worth particular attention. [Reviewed in *Rubber World*.]

BIBLIOGRAPHY OF RUBBER LITERATURE (INCLUDING PATENTS), 1949–51. Published by the Division of Rubber Chemistry of the American Chemical Society. (Order from Rubber Age, 101 West 31st Street, New York 1, New York.) Price $7.50—With the publication of this, the Ninth Edition, coverage of the rubber literature (including patents since 1950) has been accomplished for the period from 1935 through 1951. For the record, the first four of these bibliographies, covering the literature from 1935 through 1939, was published independently by *Rubber Age*, and the last five editions, including the current one, covering the literature and patents from 1940 through 1951, by the Division of Rubber Chemistry of the American Chemical Society. The current edition of the Bibliography is the second one to be issued spanning a three-year period. Once again the Bibliography is based on the rubber references prepared at the Research Center of the United States Rubber Company, plus additional references culled from *Rubber Abstracts*, the comprehensive monthly abstract journal published by the Research Association of British Rubber Manufacturers. The splendid abstract section which continues to appear in every issue of *Revue générale du caoutchouc* is another source which is quite helpful in the compilation of these editions. The style and format of previous issues has been closely followed in the current edition and again a special effort has been made to indicate where more comprehensive abstracts of any article or patent can be found, particularly those appearing in *Chemical Abstracts* and *Rubber Abstracts*. All the pertinent issues of RUBBER CHEMISTRY AND TECHNOLOGY have been carefully checked to make certain that references to the production of articles in that journal appear in connection with the bibliography references. The letter-number identification system has been continued in the current edition, while the journal abbreviation used, with a few minor exceptions, follow those established by the American Chemical Society. It is still the hope of the Bibliog-

raphy Committee that some day ten-year cumulative volumes will be issued, thus greatly simplifying any search of the rubber literature.

The Division of Rubber Chemistry is anxious to bring these bibliographies up to an annual basis as soon as possible. Unfortunately, due to a number of circumstances, publication of the current edition has been considerably delayed, with the result that the time-table established by the Bibliography Committee some three years ago has been upset. However, considerable work has already been done on the next edition, covering the period from 1952 through 1954, and unless unforeseeable obstacles arise the 1952–54 edition will be published in the spring of 1958. It should be followed in less than a year with the 1955–57 edition, which means that an annual basis could be reached by 1960. [Excerpted from the Preface by M. E. Lerner.]

TEXTBOOK OF POLYMER CHEMISTRY. Fred W. Billmeyer, Jr. Interscience Publishers, 250 Fifth Avenue, New York 1, New York. Cloth cover, 6 × 9 inches, 518 pages. Price $10.50.—As its name implies, and, according to the author's statement, this book is intended as a text for "graduate-level courses in the chemistry of high polymers." It is divided into six parts, as follows: introduction (8 pages), physical chemistry of polymers (153 pages), kinetics of polymerization (101 pages), properties of plastics (89 pages), properties of fibers (51 pages), and properties of elastomers (78 pages). The book is further subdivided into short sections (57 in all), with the applicable references listed at the end of each section, where they are readily available. This volume also contains three appendixes, viz., list of symbols, table of physical constants, and list of trade names, as well as an author and a subject index.

It is at once obvious that the author's undertaking was indeed an ambitious one, since he attempted to include not only the organic and physical chemistry of polymers, but the physical behavior aspects as well, all within the limit of 500-odd pages! The author makes no attempt to limit himself to the more elementary considerations, but includes the more advanced material as well. In view of this fact it is not surprising that the treatment accorded to each topic must perforce be very limited. The book itself can only act therefore as a "source book" of polymer chemistry for the purpose of directing the reader to the main literature sources. The material shows a good understanding of the basic principles by the author and is free of any serious errors or misconceptions.

As a textbook, it is rather breathtaking in its scope, though meager in its substance. It can, however, serve as an excellent source book, because of its wide coverage. [Reviewed by Maurice Morton in *Rubber World*.]

A GUIDE TO THE LITERATURE OF CHEMISTRY. Second Edition. E. J. Crane, Austin M. Patterson, and Eleanor B. Marr. John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, New York. Cloth cover, 6 × 9 inches, 408 pages. Price $9.50.—No chemist can possibly know all of chemistry, but he can know how and where to look for chemical information. The Second Edition of the Guide provides an effective key to the vast chemical literature of today. The First Edition of this book by E. J. Crane, director and editor of the Chemical Abstracts Service of the American Chemical Society, and the late Austin M. Patterson, former professor of chemistry at Antioch College, was published in 1927. The Second Edition is primarily the work of Eleanor B. Marr, assistant professor of chemistry at Hunter College, New York. As Dr. Crane states in the foreword, while Dr. Marr is now the principal author, the

authors of the First Edition, with appreciation of her work, have contributed enough from their wide experience with chemical literature to make this edition in a restricted sense a three-author product.

In essence this edition of the Guide (1) contains the most frequently used information, (2) gives sources where additional information can be found, (3) gives sources of less frequently used information, and (4) points out methods whereby one can keep up to date on literature and methods of using it. The first chapter discusses the problem and objectives, the second covers books, the third periodicals, the fourth patents, the fifth government publications, the sixth trade literature, and the seventh other sources. Chapter eight deals with indexes, nine with libraries, and ten with procedure in literature searches. Extensive appendixes cover such things as symbols, abbreviations, and standards used in chemical literature; a bibliography list of periodicals, scientific and technical organizations; and dealers and publishers. [Reviewed in *Rubber World*.]

RUBBER: FUNDAMENTALS OF ITS SCIENCE AND TECHNOLOGY. Jean Le Bras. Translated by Irene E. Berck. Chemical Publishing Company, 212 Fifth Avenue, New York 10, New York; Book Department, Rubber Age, 101 West 31st Street, New York 1, New York. Cloth cover, $5\frac{1}{2} \times 8\frac{1}{2}$ inches, 464 pages. Price $12.00.—The rubber manufacturing industry has long been in need of a textbook, one which would serve not only the embryo rubber chemist but the experienced technologist and the practical chemist as well. This is the first book in the English language which answers that need. It is written in a simple and direct style to make it interesting and easy to grasp. Complicated theoretical considerations, such as the reinforcement of rubber, are avoided, but the more important aspects, including the chemical structure of rubber and the theories of vulcanization, are discussed in considerable detail.

How extensively the book covers its ground is best indicated by the titles of its 15 chapters. These are: (1) General aspects; (2) Sources and preparation of natural rubber; (3) The composition and properties of latex; (4) The physical properties of rubber; (5) The chemical composition and structure of rubber; (6) The chemical properties of rubber; (7) Vulcanization; (8) Compounding ingredients and their application; (9) Processing of rubber; (10) Direct application of latex; (11) Theoretical aspects of rubber chemistry; (12) Synthetic rubbers; (13) Analyses and tests for latex and rubber; (14) Hard rubber, reclaimed rubber and chemical rubber derivatives; (15) Applications of rubber. In addition, there is a general bibliography, a list of periodicals devoted to rubber, and a cross-reference subject index.

Actually, this book has been in the making for almost 16 years. In 1941, the French Rubber Institute asked Dr. Le Bras to organize a training course for rubber engineers and technicians. The course which was eventually conceived covered the fundamentals of the science and technology of rubber in the simplest and clearest possible style. Due to popular demand the course material was compiled and organized in book form and issued in a French edition in 1951, with a second edition in 1953. The American book is a translation of the 1953 edition with a good deal of new information added to bring it completely up-to-date. Dr. Berck's translation is amazingly accurate and a special effort was made to incorporate illustrations depicting the American counterparts of most of the European photographs. Some 190 illustrations are used. [Reviewed in *Rubber Age* (N. Y.).]

Die Physik der Hochpolymeren. Edited by H. A. Stuart. Volume IV. Theorie und Molekulare Deutung Technologischer Eigenschaften von Hochpolymeren Werkstoffen. J. P. Berry, J. D. Ferry, E. Jenckel, W. Kast, H. F. Mark, W. Meskat, O. Rosenberg, F. Schwarzl, A. J. Staverman, R. S. Stein, H. A. Stuart, H. Thurn, L. R. G. Treloar, A. K. van der Vegt, and F. Würstlin. Springer-Verlag, Reichpietschufer 20 (West-Berlin), Berlin W 35, Germany. Price $21.22.—This massive work on the physics of high polymers is completed by the appearance of this volume which maintains the standards set by its predecessors. The eminence of the contributors—English, American, German, and Dutch—ensures the quality of the work. As in the previous volumes the expert hand of Professor Stuart can be readily detected in the arrangement of the material and the absence of overlap between even closely allied topics. The field covered is necessarily a wide one starting with a very fine discussion of linear and nonlinear deformation phenomena and developing to consideration of the relation of structure to a number of physical properties, e.g., mechanical and electrical, of high polymers. The mathematical arguments are lucidly explained and the experimental material and relevant data pointedly chosen.

In addition to Chapters 1 and 2, Linear and Non Linear Deformation Behavior of High Polymers, respectively, Chapters 5 and 6, The Structure and Mechanical Properties of Rubberlike Materials and of Plastics, respectively, and Chapter 7, Part B, Creep and Relaxation of Fibers, are presented in English. This makes a total of 318 pages in English as compared to only 331 pages in German. [Reviewed in *Transactions of the Faraday Society*.]

Polymer Solutions. H. Tompa. Academic Press, Inc., 125 East 23rd Street, New York 10, New York. Cloth cover, 5½ × 8½ inches, 325 pages. Price $8.50.—This book deals with the theories of polymer solutions, and with the information concerning molecular properties (size, weight, and intermolecular interactions) which can be deduced from thermodynamic data through the use of such theories. Each topic is approached from the viewpoint of theory, the pertinent relationships are set down or derived, and the forthcoming conclusions are discussed. This is followed by selected examples of experimental data chosen to illustrate or test particular features of the theories. Among the measurements considered by the author are vapor pressure and calorimetry, osmotic pressure, viscosity and light scattering, but not sedimentation and flow birefringence. The reader will find that while considerable progress has been made on the problem of the configurational entropy gain on mixing, rather less success has been met in treating intermolecular interactions. For this reason the author restricts his attention to nonpolar mixtures whenever possible. Polyelectrolytes are not included.

The reviewer heartily recommends this book to those interested in a survey of the present status of the thermodynamics of polymer solutions. Although the author is at his best in those topics most closely connected with his own research efforts, the entire exposition is stimulating and exceedingly clearly written. [Reviewed by William R. Krigbaum in *Journal of Polymer Science*.]
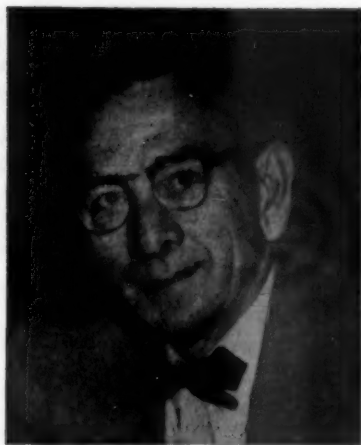
## ARTHUR M. NEAL

With the death on April 18, 1957, of Arthur M. Neal, the Division of Rubber Chemistry lost an ardent supporter and the fraternity of rubber chemists and technologists an effective contributor to the advancement of the science of rubbers.

Born in West Boylston, Massachusetts, on July 11, 1902, he received his AB and MA degrees from Clark University in 1923 and 1924 respectively. In 1927 he received his PhD in Chemistry from Brown University. After graduation he joined the Grasselli Chemical Company at its Cleveland, Ohio, laboratories and shortly thereafter joined Du Pont as a research chemist at the Jackson Laboratory. From 1929, when he joined Du Pont, until his death he was associated in various capacities with work in the field of the chemistry and technology of rubbers. His final position was that of assistant director of Elastomers Laboratory at Chestnut Run.

His published papers and patents were concerned principally with the field of rubber chemicals, their preparation, evaluation in rubber and their mode of action. Of 26 U. S. patents 24 are in this field, and of 17 technical publications 16 are in this field. However, his interests in rubber were broader than is indicated by this listing. He was co-author of the excellent chapter on neoprene in Synthetic Rubber, edited by Whitby, he was granted one patent on reclaiming, one on an adhesive cement, and in discussions it was evident that his interests covered the broad field of rubber science.

One of his important activities was his participation in the affairs of the Division of Rubber Chemistry and the American Chemical Society. He was a director of the division from 1946–1948, councillor representing the division from 1949 until his death, and secretary from 1954 until his death. He was a member and secretary of the standing committee of the ACS on National Meetings and Divisional Activities.

He was the kind of person who devoted himself whole heartedly and unstintingly to these assignments and his experience and knowledge of the affairs

of the ACS as well as of the Division of Rubber Chemistry was of enormous benefit both to the parent society and the division. The clarity of his thinking, his ability to state the facts in a case, and to suggest methods of overcoming obstacles were demonstrated time and again in sessions of the Executive Committee of the division.

He was a member of Lambda Chi Alpha and Sigma Xi fraternities. He was an active member of the Second Baptist Church in Wilmington, and was serving on its board of trustees at the time of his death. He was also active in the Boy Scout movement. He was an ardent and expert bridge player, and had participated in numerous tournaments.

A. E. Juve

# DETERMINATION OF THE MOLECULAR SIZE AND THE MOLECULAR FORM OF NATURAL RUBBER BY THE MEASUREMENT OF LIGHT SCATTERING. I. DEVELOPMENT OF THE METHOD AND ORIENTING MEASUREMENTS *

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## INTRODUCTION

We know from the investigations of Carter, Scott and Magat[1], as well as those of Bloomfield[2], that the molecular weight of rubber harvested under careful conditions lies in the order of magnitude of one to two million. Bloomfield's fractionation experiments have shown further that the sol part of the rubber is molecularly nonuniform and that the average molecular weight and the distribution curve vary according to origin. We owe these data principally to the osmotic method. However, the latter is not very accurate within the range of magnitude involved here (due to the small effect) and furthermore, because of the relatively long adjusting period, exclusion of the action of the oxygen creates great difficulties. It therefore seemed promising to us to apply the method of light scattering to rubber solutions. In the field of synthetic and some natural polymers this method has led to important advances.

In this connection another problem can be tackled at the same time, namely the question of the shape of the rubber molecule and of the influence which storage and other actions of various kinds have on this property. We know that in synthetic polymers, the molecules are more or less branched and that important physical and technological properties depend on them. On the basis of Debye's theory, besides the molecular weight the spatial dimensions of dissolved molecules may be determined by light scattering measurements, which dimensions, in filamentary molecules, are a function not only of the internal mobility but also of the degree of branching.

The more branching sites a filamentary molecule possesses, the more densely packed coil form it assumes in solution. In order to be able to draw conclusions about the degree of branching from the optically measured coil diameters, it must nevertheless be kept in mind that the solvent also has an influence on the coil dimensions[3,4,5,6]; for this reason there are still considerable difficulties in setting up an exact theory about the relationship between coil dimensions and branching[7]. It appears promising, nevertheless, to come closer to the solution of this problem through a comparison with synthetic polymers for which we have more experimental results at our disposal. In doing so one may, as will be shown further below, start from the working theory that unbranched filamentary molecules of the same number of chainlinks and analogous steric structure possess the same coil diameter in solvents with the same 2nd virial coefficient $B$.

From this follows the necessity of carrying out a thorough thermodynamic analysis of the solution systems used. While in the past osmotic measurements were principally used for this purpose, this can now be attained[8] more simply and more comprehensively by measurements of light scattering, as one of us showed recently[9].

In this paper we report on experiments, the principal purpose of which was to work out the experimental methodology and to obtain at the same time orienting results from which the direction of future work would follow. We used a "purified crepe rubber" from the Indonesian Rubber Research Institute at Bogor. There the latex was tapped with exclusion of air and light, and purified by means of soap displacement and centrifuging and, after stabilization, coagulated with Vulkastab LW. The analysis gave 0.05% $N_2$; 0.05% ash and 1.66% acetone extract. It was stored at $-15°$ C under nitrogen.

### EVALUATION OF THE LIGHT SCATTERING MEASUREMENTS WITH REGARD TO MOLECULAR WEIGHT, COIL DIAMETER AND THERMODYNAMIC PROPERTIES OF THE SOLUTION

The equations used in the evaluation of the light scattering measurements are briefly assembled in what follows. The quantity of measurement is the molecular scattered light $R_\vartheta$, i.e., the intensity of the scattered radiation in the unit volume with unit distance for the primary radiation intensity 1. It is a function of the observation angle $\vartheta$ and the wavelength $\lambda$. It stands in the relation derived by Debye to the molecular weight $M$ and the concentration $C$ of the polymer

$$\frac{Kc}{R_\vartheta} = \frac{1}{MP_\vartheta} + \frac{2Bc}{RT} + \frac{3Cc^2}{RT} + \cdots \tag{1}$$

($R$ = gas constant, $T$ = absolute temperature). $B$ and $C$ are the virial coefficients of osmotic pressure $\Pi$ corresponding to the series

$$\frac{\Pi}{c} = \frac{RT}{M} + Bc + Cc^2 + \cdots \tag{2}$$

Constant $K$ to be determined experimentally for each solution system is for vertically polarized primary light

$$K = \frac{4\pi^2 n_1^2}{N_L \lambda_0^4} \left(\frac{dn}{dc}\right)^2 f \tag{3}$$

($n_1$ = refractive index of the solvent; $dn/dc$ = refraction increment of the solution; $N_L$ = Loschmidt number; $\lambda_0$ = wavelength in vacuum; $f$ = Cabannes' factor).

Scatter function $P_\vartheta$ permits the determination of the spatial dimension of the molecules; when the molecules are small in comparison with the wavelength ($< \lambda/20$) then $P_\vartheta = 1$. For layer molecules $P_\vartheta < 1$ for all angles except $\vartheta = 0$. It is derived from the dependence of the scattering radiation on the angle in the following manner. When $Kc/R_\vartheta$ is plotted against function

$$\left(\sin^2 \frac{\vartheta}{2} + 100\ c\right)$$

in the so-called Zimm diagram a two-dimensional series of measuring points is formed which can be extrapolated for the angle $\vartheta = 0$ and the concentration $c = 0$ (see Figure 6).   Both extrapolation curves cross on the ordinate axis. Due to $P_0 = 1$ the ordinate intercept is

$$\lim_{\substack{\vartheta=0 \\ c=0}} \frac{Kc}{R_\vartheta} = \frac{1}{M} \tag{4}$$

This extrapolation thus gives the *molecular weight* $M$ directly.   It is particularly important for the reason that in this manner one is free of any assumption about the molecule form, respectively the thermodynamic properties of the solvent.

The *molecular dimensions* are obtained from the dependence of scatter function $P_\vartheta$ on the angle either by direct evaluation of the Zimm diagram or more simply from the asymmetry:

$$Z = \frac{R_{45}}{R_{135}}$$

The relationship between the end to end distance of statistical coils and these two measurement quantities have been calculated by Debye[10] and Zimm[11] and have been tabulated, e.g., in Houben-Weyl, Methoden der Organischen Chemie[12].

For the thermodynamic characterization of the solution one starts appropriately with Equation (1) multiplied by $RT$ as then the rise in the graphic representation is directly connected with the virial coefficients:

$$\frac{RT\,Kc}{R_\vartheta} = \frac{RT}{MP_\vartheta} + 2Bc + 3Cc^2 + \cdots \tag{1a}$$

If one separates the osmotic pressure of the solution into the two parts:

ideal osmitic pressure

$$\Pi^* = \frac{RT}{M} c \tag{5a}$$

and supplementary pressure

$$\Pi^E = BC^2 + Cc^3, \tag{5b}$$

so that

$$\Pi = \Pi^* + \Pi^E \tag{5c}$$

then one sees at once that in Equation (1a)

$$\frac{RT}{MP_\vartheta} = \frac{\partial \Pi^*}{\partial c} \cdot \frac{1}{P_\vartheta}$$

and

$$2\,Bc + 3\,Cc^2 = \frac{\partial \Pi^E}{\partial c}$$

and thus

$$\frac{RT\,Kc}{R_\vartheta} = \frac{1}{P_\vartheta} \frac{\partial \Pi^*}{\partial c} + \frac{\partial \Pi^E}{\partial c} \tag{6}$$

Multiplication of the osmotic pressure with the partial molecular volume of the solvent $\bar{v}_1$ gives the chemical potential of the solvent

$$\Delta\mu_1 = -\bar{v}_1\Pi \tag{7a}$$

$$\Delta\mu_1{}^* = -\bar{v}_1\Pi^* \tag{7b}$$

$$\Delta\mu_1{}^E = -\bar{v}_1\Pi^E \tag{7c}$$

when we divide also $\Delta\mu_1$ into the ideal part $\Delta\mu_1{}^*$ and the supplementary part $\Delta\mu_1{}^E$ corresponding to

$$\Delta\mu_1 = \Delta\mu_1{}^* + \Delta\mu_1{}^E \tag{8}$$

From the Zimm diagram the quantities $M$, $P_\theta$, $C$, $C$, etc., by which a solution system is characterized at a certain temperature, are obtained directly. Therefore, we are also able to calculate $\Pi/c$ in accordance with Equation (2) as a function of the concentration (see Figure 9).

When the scattering intensity is measured at several—at least two—temperatures one can calculate also the heat of dilution and entropy of dilution as a function of the concentration. It has been shown by one of us[9], one can start again with the quantities $B$ and $C$ with which to be true, for practical reasons, one arrives only at clear relationships when the 3rd virial coefficient $C$ can be neglected. In this case equations are used which Reik and Gebert have derived. We have

$$\Delta\mu_1{}^E = -B\,\bar{v}_1\,c^2 \tag{9a}$$

the differential heat of dilution

$$\Delta h_1 = -\left(B - T\frac{\partial B}{\partial T}\right)c^2\,\bar{v}_1 \tag{9b}$$

and the differential supplementary entropy of dilution

$$\Delta s_1{}^E = c^2\,\bar{v}_1\frac{\partial B}{\partial T} \tag{9c}$$

which stand to each other in the Gibbs-Helmholtz relationship.

$$\Delta\mu_1{}^E = \Delta h_1 - T\Delta s_1{}^E \tag{10}$$

The path just described first determines from the light scattering data the virial coefficients and uses them for the calculation of the thermodynamic quantities $\Delta H_1$ and $\Delta s_1$. However, in many cases it is more appropriate to determine from the light scattering values measured, first the thermodynamic quantities $\Pi$, $\Pi^E$, $\Delta\mu_1$, $\Delta\mu_1{}^E$ for each concentration and then to calculate the heat of dilution and the entropy of dilution from their temperature dependence for each concentration.

Next one must integrate Equation (6) for the individual points measured. Equation (11) for the osmotic auxiliary pressure is thus obtained since $\Pi^*$ can be calculated from (5a) when the molecular weight is known:

$$\Pi^E = RT\left(\int_0^c \frac{Kc}{R_\theta}\,dc - \frac{c}{M\,P_\theta}\right) \tag{11}$$

The chemical potential is then obtained from Equations (7a) to (7c).

The integration can be carried out very easily as only directly measurable quantities are shown on the right hand side and the expression between brackets vanishes for $c = 0$ (see Section IV c).

When one has determined in this manner $\Delta\mu_1{}^E$ for several—at least two—temperatures, then the supplementary entropy of dilution is obtained by means of the general thermodynamic equation

$$\Delta s_1{}^E = -\,\partial\Delta\mu_1/\partial T \tag{12}$$

and the heat of dilution from

$$\Delta h_1 = \frac{\partial(\Delta\mu_1/T)}{\partial(1/T)} \tag{13}$$

A check is furnished in that the calculated values of $\Delta h_1$ and $\Delta s_1$, respectively, $\Delta s_1{}^E$ must be independent from the wavelength.

The relationships derived above are rigorously valid only for solutions of molecularly uniform substances. In the case of polymolecular substances the light scattering gives the weight average of the molecular weight $(M_w)$, however, the osmotic pressure gives the low numerical average $(M_n)$. Therefore, in Equation (1a) the exact $M_w$ is to be used, however in Equation (5a) $M_n$ is to be used. If according to (5a) we calculate $\Pi^*$ using the $M_w$ value obtained from light scattering too low values are obtained. How large the error caused by this cannot be stated as yet, since we do not know the nonuniformity of our rubber sample. The supplementary quantities $\Pi^E$, $\Delta\mu_1{}^E$, $\Delta s_1{}^E$, and $\Delta h_1$ are not affected by this neglect, so that the thermodynamic characterization undertaken below of the rubber-cyclohexane solution system is theoretically correct.

## EXPERIMENTAL METHOD AND EVALUATION OF THE MEASUREMENTS

*Preparation of optically homogeneous rubber solutions.*—In the preparation of rubber solutions two things must be watched, especially: First, during the solution process oxygen must be absent so that one retains the natural material as close as possible. Second, all gel and microgel components must be removed from the solution as otherwise the light scattering method is not applicable.

There are principally three possibilities which would allow an attack by the oxygen on the rubber molecule:

1. When the solvent contains dissolved oxygen or peroxides,
2. When air is absorbed by the rubber sample,
3. When air gets at the finished solution.

To eliminate the first possibility we have heated the solvent to boiling several times over sodium in a stream of $N_2$ and distilled it in a stream of $N_2$. The last distillation was carried out in special equipment (Figure 1). Before introducing the solvent the apparatus was evacuated and filled with osram nitrogen ($O_2$ content less than $10^{-4}$ per cent). During the distillation $N_2$ is blown through the capillary and after the distillation is finished through stopcock 1. In this manner the receiver can be removed after the distillation without the air getting into the interior of the receiver. Ground joint 2 is closed and ground cap 3 is exchanged for a ground joint with attached stopcock. The receiver now serves as a storage container for the solvent. A slight excess nitrogen pressure is applied to it so that for the withdrawal it is only necessary to open stopcock 4. The solvent flows out under the excess pressure.
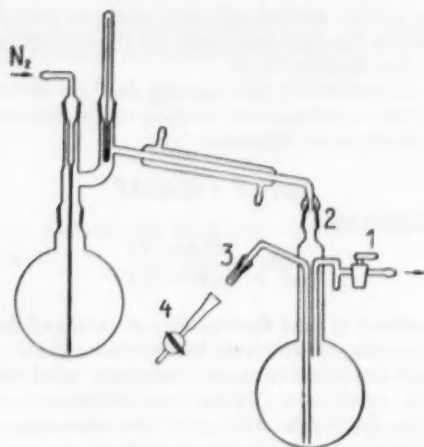
Fig. 1.—Distillation apparatus.

The dissolving of the rubber is carried out under high vacuum.  Special apparatus was also developed for this purpose.  With the arrangement shown in Figure 2, three solutions can be prepared at the same time.  Pumps 1, 2 and 3—respectively, an oil centrifugal pump, an oil vapor jet pump and an oil diffusion pump—can be connected, singly or in combination, to the distribution system 7 through stopcocks 4, 5, and 6.  Already pumps 1 and 2 produce a vacuum of $10^{-5}$ mm. Hg, when oil diffusion pump 3 is connected, $5 \times 10^{-6}$ mm. Hg is reached.  The vacuum was measured with the Moser manometer 8. Tubing 9 leads to the osram nitrogen tank; pipe 10 serves as excess pressure valve and at the same time as manometer for vacuums up to 1 mm.  To header system 7 three tubes 12 are connected with mercury closures through cold trap 16.  To tubes 12 the flasks containing the rubber are fused by means of "fusing tubing", i.e., by means of thickwalled very constricted tubing.  Next the flasks containing the rubber are evacuated several times to $10^{-5}$ mm. Hg, while flushing with nitrogen in between.  In this manner the greatest part of the air ab-
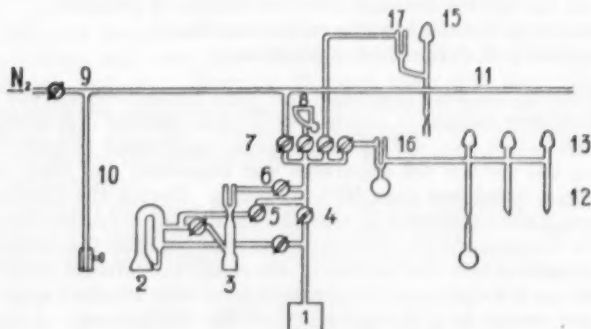


Fig. 2.—High vacuum apparatus for the preparation of rubber solutions.

Fig. 3.—Mercury closure.

sorbed on the rubber is removed and exchanged for nitrogen. Now at slight excess nitrogen pressure the mercury closures 13, which are shown more accurately in Figure 3, open and through them the flasks are provided with solvent. The flasks are then cooled to $-78.6°$ with $CO_2$-acetone mixture and the cold trap 16 is filled with the same mixture. The system is then evacuated with pumps 1 and 2. After threefold evacuation and flushing with nitrogen, the flasks are fusion closed at high vacuum at the fusion points and removed from the apparatus set-up. Only then the solution process follows.

A flask, filled in the manner described is placed in a thermostat which rests upon a magnetic stirrer. In it the rubber is, in general, dissolved at $25°$ C by stirring. The dissolving process is completed in 2–6 hours depending on the solvent and the dissolving temperature.

The optical purification of the solutions was carried out by centrifuging. Filtering through glass frits was shown to be unsuited because of preferential absorption of the high molecular weights. It was shown also that a sufficient optical purification of the solution is achieved only by the use of a very strong centrifugal field. Therefore, we used a preparative Spinco ultracentrifuge and worked with an acceleration of 100,000 g. (30,000 revolutions/min.). The result for four solvents is shown in Table I.

The viscosity numbers were measured in Ostwald viscometers operated with $N_2$ with a velocity gradient of 600 sec.$^{-1}$. They lie in the same order of magnitudes as Bloomfield's values[2].

We determined the concentrations by evaporation of the solutions at $60°$ first at normal pressure, and then under vacuum to constant weight. In general, the accuracy is better than $\pm 1$ per cent.

TABLE I

PART CENTRIFUGED OFF IN VARIOUS SOLVENTS AND VISCOSITY
NUMBER OF THE SOL PART

| Solvent | Centrifuging temperature, °C | Centrifugate approximation values, % | $[\eta]$ in cm.$^3$ g$^{-1}$ |
|---|---|---|---|
| Cyclohexane | +15 | 40 | 245 |
| Benzene | +15 | 3 | 560 |
| Toluene | +15 | 1 | 615 |
| Cyclohexene | -10 | 6 | 595 |
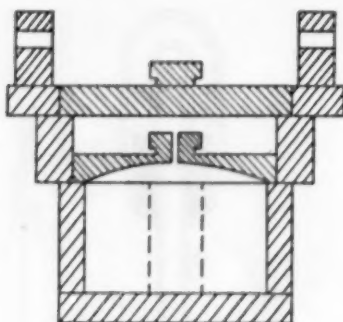
Fig. 4.—Scattered light cell.

*Optical measurements.*—As appears from Debye's Formulas (1) and (3), the refractive indexes of solvents $n_1$ and the refraction increments of the dissolved rubber $dn/dc$ are used for the evaluation of the molecular light scattering. These optical data were measured in a differential refractometer as per Schultz, Bodmann and Cantow[13], which was improved by Bodmann[14] in the meantime.

The measurements were made, in general, at 25° C, and only for cyclohexene at 27° and 7°. The values obtained at the wavelengths of 4350, 5530 and 5740 Å were recalculated to the wavelengths 5461 and 4358 Å, used in the light scattering measurements, by means of the Hartmann dispersion paper.

The scattered light measurements were made in Cantow's[15] scattered light photometer in which the observation angle $\vartheta$ varies continuously between 30 and 150° and the temperature can be regulated up to 50° C. The benzene values, determined by one of us[16] recently, served as a scattering standard. They lie with $R_{90} = 15.4 \times 10^{-6}$ cm.$^{-1}$ for 5460 Å and $R_{90} = 44.0 \times 10^{-6}$ cm.$^{-1}$ for 4360 Å closely below those of Carr and Zimm. The corrections in refraction according to Hermans and Levinson were taken into consideration[17].

The cylindrical cells hold 10 cc. of solution. As may be seen from Figure 4 they are equipped with two covers, the lower one of which is made of black glass and is ground in spherical cup form and has a fine drill hole in the center. It dips into the upper part of the solution and eventual gas bubbles escape into the space above this cover so that the solution in the measuring space is relatively well protected against access of air.

The cells are cleaned and rendered dust-free by means of a cleaning apparatus as described by Thurmond[18].

Thus far the optimum temperature spread for the scattered light measurements lies between 7 and 27° C. Above that, decomposition takes place too rapidly, below it the cells mist up too easily due to atmospheric moisture.

## TABLE II

### REFRACTIVE INCREMENTS OF UNFRACTIONATED CREPE RUBBER IN VARIOUS SOLVENTS AND THE REFRACTIVE INDEXES OF THE SOLVENTS AT 25° C

| Solvents | $dn/dc$ 5461 Å | $dn/dc$ 4358 Å | $n_1$ 5461 Å | $n_1$ 4358 Å |
|---|---|---|---|---|
| n-Hexane | 0.1802 | 0.1886 | 1.3740 | 1.3805 |
| Chloroform | 0.095 | 0.100 | 1.4433 | 1.4525 |
| Toluene | 0.0339 | 0.0308 | 1.4963 | 1.5131 |
| Cyclohexene | 0.0943 | 0.0988 | 1.4425 | 1.4521 |

This latter disadvantage is not basic in nature and will be removed in the fore-
seeable future.   The methodology was such that measurements were made
first at 7° C, then at 27° C, then again at 7° and once more at 27° C.   The
second measurement at 27° C showed deviations occasionally compared with
the first and in that case was not considered in the evaluation.   The two meas-
urements at 7° C were in good agreement.   The work was carried out at two
wavelengths: 5461 Å and 4358 Å.   The values obtained with green light showed
a smaller range of error than those obtained with violet light.

## THE RESULTS OF THE MEASUREMENTS

*Determination of the refractive increments and of constant K according to
Equation* (3).—The refraction data measured at 25° C for 4 solvents are shown
in Table II.   It may be seen that the refractive increment of rubber in toluene
is especially small so that scattered light measurements in such solutions is
subject to considerable errors.   Benzene is even less favorable as solvent, in
this connection.   Solutions of rubber in chloroform show, indeed, a good re-
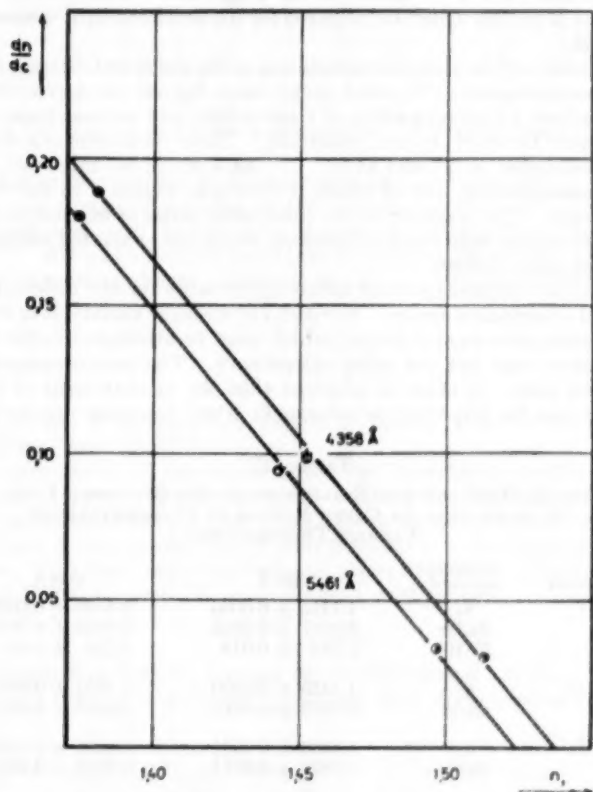
FIG. 5.—Dependence of the refractive increment of rubber on the refractive index of the solvent.   ●
n-Hexane, + Chloroform, ○ Cyclohexene, ◑ Toluene.

fractive increment but cannot be purified by centrifugation because of the higher density of chloroform. Among the solvents investigated only cyclohexene remains since in $n$-hexane the gel portion is too high. As a result, the measurements described in what follows were carried out on solutions of the unfractionated crepe rubber.

In Figure 5 the refractive increments of the rubber in various solvents are plotted against the refractive indexes of the corresponding solvent. For the wavelengths of 5461 and 4358 Å, approximately two straight lines are obtained in agreement with the known rule of Gladstone and Dale.

Due to the thermodynamic evaluation, scattered light measurements were carried out at various temperatures. For this, measurements were also required of the optical data at various temperatures, as both $n_1$ and $dn/dc$ vary with temperature.

In Table III the refractive indexes of cyclohexene and the refractive increments of crepe rubber in this solvent, at various temperatures and wavelengths, have been assembled. The values at 27° and 17° C were obtained from several measurements by approximation to the mean, those for 25° and 7° C were calculated from it by means of the temperature dependency. For 27° and 7° C the $K$ values, which are required for the scattered light measurements, are included.

*Determination of the molecular weight and of the end to end distance from scattered light measurements.*—We used cyclohexene for our measurements as this solvent dissolved a high proportion of crepe rubber and because these solutions have relatively favorable optical constants. These measurements were made at two wavelengths, at 7° and at 27° C. As a whole we thus obtained four series of measurements, one of which is shown in Figure 6 in the form of a Zimm diagram. The diagrams of the three other series of measurements differ from that shown by only small differences, which are evaluated arithmetically in the tables which follow.

The accuracy of measurement differs appreciably for the different concentrations and observation angles. For $\vartheta < 75°$ stronger variations in the results of the measurements were obtained, which must be attributed to the fact that the purification was not yet quite satisfactory. The measurements at $\vartheta = 90°$ were the best. It must be assumed that the measurement of the angle dependence can be improved substantially when fractions are used. As a

TABLE III

OPTICAL DATA FOR THE EVALUATION OF THE SCATTERED LIGHT
MEASUREMENTS ON CREPE RUBBER IN CYCLOHEXANE AT
VARIOUS TEMPERATURES

| Temperature | Quantity measured | 5461 Å | 4358 Å |
|---|---|---|---|
| 27° C | $n_1$ | 1.4415 ± 0.0006 | 1.4509 ± 0.0007 |
| | $dn/dc$ | 0.0947 ± 0.0013 | 0.0992 ± 0.0012 |
| | $K \cdot 10^7$ | 1.374 ± 0.019 | 3.764 ± 0.05 |
| 25° C | $n_1$ | 1.4425 ± 0.0006 | 1.4521 ± 0.0007 |
| | $dn/dc$ | 0.0943 ± 0.0013 | 0.0988 ± 0.0012 |
| 17° C | $n_1$ | 1.4466 ± 0.0004 | 1.4567 ± 0.0007 |
| | $dn/dc$ | 0.0909 ± 0.0014 | 0.0953 ± 0.0013 |
| 7° C | $n_1$ | 1.4519 ± 0.0006 | 1.4622 ± 0.0007 |
| | $dn/dc$ | 0.0869 ± 0.0015 | 0.0914 ± 0.0014 |
| | $K \cdot 10^7$ | 1.173 ± 0.021 | 3.244 ± 0.05 |
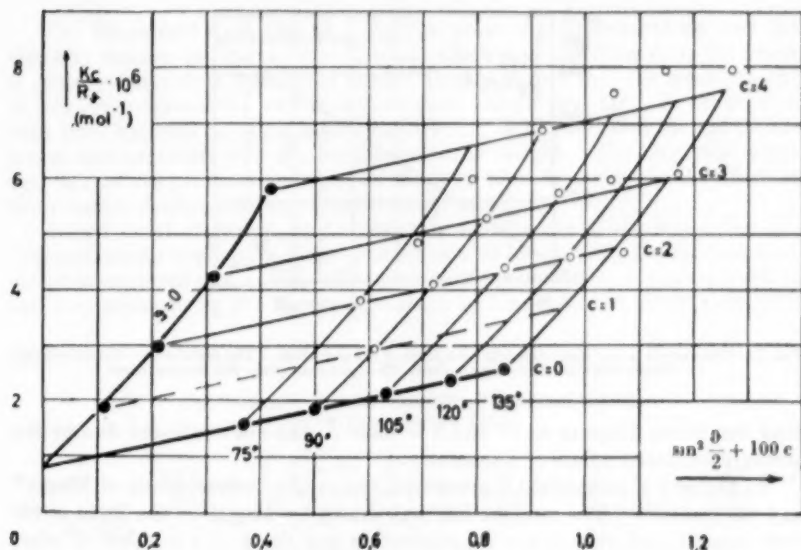
FIG. 6.—Zimm diagram of rubber in cyclohexene at 27° C for the wavelength $\lambda_0 = 5461$ Å.

whole the reproducibility is the best at a concentration of 2 g./l. The line system was, therefore, adapted for the curves at a constant angle of the measuring series at $\vartheta = 90°$ and for a constant concentration of the measuring series at $c = 2$. Also the condition holds that the limiting curves for $c = 0$ and $\vartheta = 0$ must cross on the ordinate. Because of this the ordinate intercept

$$\left[ \frac{Kc}{R\vartheta} \right]_{\substack{c=0 \\ \vartheta=0}}$$

and, therefore, $M$ are determined quite accurately, even though extrapolation over a fairly long stretch is involved.

The evaluation of the experiments was undertaken on the basis of the Equations (1), etc. The asymmetries could not be obtained, as is customary, by extrapolation of the quotient $R_{45}/R_{135}$, calculated for each concentration, to $c = 0$; here $Z$ was obtained every time from the $c = 0$ straight line of a Zimm diagram. In view of what has been said above, the numercial values assembled in Table IV have a probable error of about ±20 per cent. It should be noted

TABLE IV

MOLECULAR WEIGHT, DEGREE OF POLYMERIZATION AND END TO END
DISTANCE $h_{si} = (\bar{h}^2)^{\frac{1}{2}}$ FROM THE FOUR ZIMM DIAGRAMS

| $T,$ °C | $\lambda_0$ [Å] | $P_M$ | $Z$ | $M_\omega$ | $P_\omega$ | $h_{si}$ [Å] |
|---|---|---|---|---|---|---|
| 27 | 5461 | 0.416 | 2.41 | $1.3 \cdot 10^6$ | 19,100 | 1750 |
| 27 | 4358 | 0.295 | 3.00 | $1.2 \cdot 10^6$ | 17,700 | 1800 |
| 7 | 5461 | 0.428 | 2.36 | $1.3 \cdot 10^6$ | 19,100 | 1700 |
| Average values: | | | | $1.3 \cdot 10^6$ | 19,000 | 1750 |
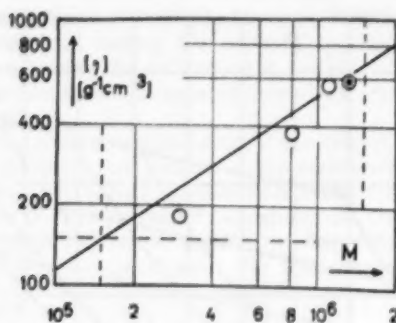
Fig. 7.—Comparison of our measurements with those of other authors. The line drawn—Magat's curve; ○—Bloomfield's osmotic measurements; ⊙—light scattering, this investigation.

that the Zimm diagram at 7° and $\lambda$ = 4358 Å was not evaluated due to the strongly scattered points of measurement.

In Figure 7 a comparison is given with the earlier measurements of Magat[19] and Bloomfield[20]. The straight line was drawn by Magat on the basis of his own osmotic and viscometric measurements and those of a number of other authors. It follows the equation

$$[\eta] = 5.02 \cdot 10^{-4} \, M^{0.67}$$
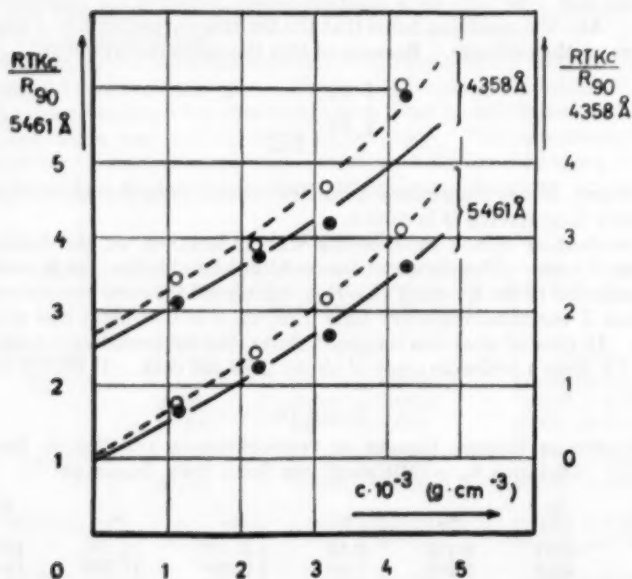


Fig. 8.—Scattering values at 2 wavelengths and 2 temperatures.  ○—27°; ●—7°.

The Bloomfield data also fit. For our point of measurement we used the viscosity number in benzene (see Table I) which does not differ from the value in cyclohexene within the limit of error. It may be seen that the measurement of this investigation fits well into the values known thus far. In connection with this, it should be taken into consideration, to be sure, that the light scattering measurements give $M_w$ for the molecular weight. The numerical average, $M_n$, of our preparation might be shoved a little to the left in the diagram since we are dealing with an unfractionated product.

*Second virial coefficient, heat of dilution and entropy of dilution.*—For the thermodynamic evaluation of the experiments we use suitably the light scattering measurements at $\vartheta = 90°$. The measurement values for two temperatures and two wavelengths are shown once more in Figure 8. In accordance with

TABLE V

CALCULATION OF THE OSMOTIC PRESSURES FROM
SCATTERED LIGHT DATA

| $c \cdot 10^4$ [g./cm.³] | $\frac{RT\,Kc}{R_{90}} \cdot 10^3$ Measured [cal mole⁻¹] | $\int_0^c \frac{Kc}{R_{90}} dc \cdot 10^4$ Equation (15) [cal mole⁻¹ g. cm.⁻³] | $\frac{RT\,c}{MP_{90}} \cdot 10^4$ [cal mole⁻¹ g. cm.⁻³] | $\Pi^E \cdot 10^4$ Equation (11) [Atm.] | $\Pi^* \cdot 10^4$ Equation (11a) [Atm.] | $\Pi \cdot 10^4$ Equation (5c) [Atm.] |
|---|---|---|---|---|---|---|
| | | 7° C; $\lambda_0 = 5461$ Å | | | | |
| 0 | 1.003 | 1.48 | 1.12 | 0.14₉ | 0.19₃ | 0.35 |
| 1.115 | 1.65 | 3.66 | 2.24 | 0.59₆ | 0.39₆ | 0.98₉ |
| 2.23 | 2.24 | 6.08 | 3.22 | 1.18 | 0.57 | 1.75 |
| 3.21 | 2.69 | 9.36 | 4.26 | 2.11 | 0.75₂ | 2.86 |
| 4.25 | 3.61 | | | | | |
| | | 7° C; $\lambda_0 = 4358$ Å | | | | |
| 0 | 1.54 | | | | | |
| 1.115 | 2.12 | 2.02 | 1.72 | 0.13₄ | 0.19₂ | 0.33₄ |
| 2.23 | 2.76 | 4.68 | 3.44 | 0.51₄ | 0.09₆ | 0.91 |
| 3.21 | 3.20 | 7.60 | 4.95 | 1.10 | 0.57 | 1.67 |
| 4.25 | 4.93 | 11.83 | 6.55 | 2.19₄ | 0.75₄ | 2.95 |
| | | 27° C; $\lambda_0 = 5461$ Å | | | | |
| 0 | 1.105 | | | | | |
| 1.09 | 1.77 | 1.57 | 1.205 | 0.15₂ | 0.20₈ | 0.36 |
| 2.18 | 2.45 | 3.87 | 2.41 | 0.60₁ | 0.41₁ | 1.01₆ |
| 3.15 | 3.17 | 6.59 | 3.48 | 1.31 | 0.59₂ | 1.91 |
| 4.17 | 4.10 | 10.30 | 4.61 | 2.34₅ | 0.79₄ | 3.14 |
| | | 27° C; $\lambda_0 = 4358$ Å | | | | |
| 0 | 1.70 | | | | | |
| 1.09 | 2.47 | 2.77 | 1.86 | 0.16₉ | 0.20₈ | 0.37₄ |
| 2.18 | 2.92 | 5.13 | 3.71 | 0.58 | 0.41₁ | 0.99 |
| 3.15 | 3.66 | 8.32 | 5.36 | 1.22 | 0.59₂ | 1.82 |
| 4.17 | 5.06 | 12.77 | 7.10 | 2.33₅ | 0.79₄ | 3.13 |

Equation (1) the curves differ by factor $P_\vartheta$ in the denominator of the first term. The scattering of the values measured is not inappreciable; however, the calculations which follow show that the essential part of the results is not affected by it.

In Table V the osmotic pressures have been calculated from the light scattering measurements. In order not to cover up the errors in measurement the integration was not made along the adjusted curve, but progress was made from measuring point to measuring point. In doing this, the individual points of measurement were connected by straight lines, whereby no noticeable error occurs in view of the very flat curvature. If the scatter values $R_1, R_2 \cdots$, belong to the concentrations $c_1, c_2 \cdots$, then one calculates by this method the integral within the brackets of Equation (1) for the $i$-th concentration by means

TABLE VI

OSMOTIC PRESSURE AND CHEMICAL POTENTIAL

$\theta_1(7°) = 97.5; \theta_1(27°) = 101.7$

| $c \cdot 10^4$ at 17° [g. cm.$^{-3}$] | $\Pi \cdot 10^4$ [Atm.] | | $\Pi/c \cdot 10^4$ [Atm. l g.$^{-1}$] | | $\Delta\mu_1 \cdot 10^6$ [cal mole$^{-1}$] | |
|---|---|---|---|---|---|---|
| | 7° | 27° | 7° | 27° | 7° | 27° |
| 0 | | | $0.17_7$ | 0.19 | | |
| 1.1 | 0.34 | 0.37 | 0.31 | $0.33_5$ | $-0.80_5$ | −0.91 |
| 2.2 | 0.95 | 1.00 | 0.43 | $0.45_5$ | −2.24 | −2.46 |
| 3.18 | 1.71 | $1.86_5$ | 0.54 | $0.58_5$ | −4.04 | −4.59 |
| 4.21 | 2.90 | $3.13_5$ | 0.69 | $0.74_5$ | −6.85 | −7.72 |

of the sum

$$\int_0^{c_i} (Kc/R_{90}) \, dc = \sum_{c_1}^{c_i} \frac{c_i - c_{i-1}}{2} \left[ \frac{Kc_i}{R_{90(i)}} + \frac{Kc_{i-1}}{R_{90(i-1)}} \right] \tag{15}$$

in which the boundary value $\lim_{c=0} \dfrac{Kc}{R_{90}}$ belongs to concentration $c = 0$ which is most safely taken from the Zimm diagram (see Figure 7).

A check of the measuring values results from the fact that the osmotic pressures calculated at the same temperature must be independent of the wavelength. One can see from a comparison of the figures contained in the last column of Table V that this is the case within the error zone given by the scattering of the measured values. In Table VI are given the average values of the osmotic pressure for 7° and 27° C. By multiplication with $\bar{v}_1$ the chemical potential of the solvent is obtained from it.

Figure 9 shows the reduced osmotic pressure as a function of the concentration. It may be seen that with the limits of error one can represent the measured points by a straight line, that one can, therefore, neglect the 3rd virial coefficient. In addition, a series of measurements made by Bloomfield, is
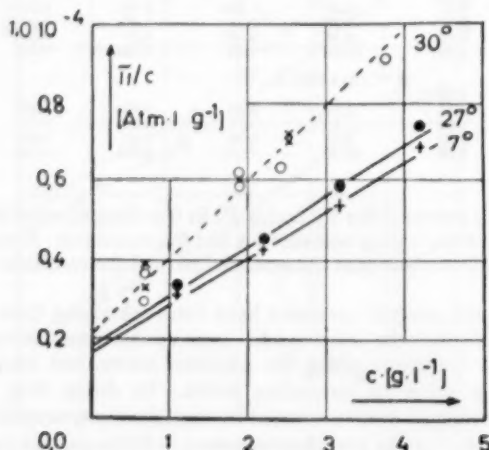


FIG. 9.—Osmotic pressure versus concentration. ●+light dispersion measurements at 27° and 7° C. $\eta$ =595 cm.³ g.$^{-1}$; O—Osmometric measurements by Bloomfield at 30° C, [$\eta$] =572 cm.³ g.$^{-1}$; x—Osmometric measurements by Bloomfield at 30° C, [$\eta$] =596 cm.³ g.$^{-1}$.

plotted in the figure; this series was determined directly osmometrically.   The viscosity numbers of the two preparations lay close to ours; the molecular weight is about 20 per cent lower.   This is due in part to the fact that Bloom-field used fractionated rubber, which is molecularly more uniform than our sample.   On the other hand, as mentioned above, the formation of the median value is different in the osmotic method from that in the scattered light method. When this is taken into consideration the agreement is quite satisfactory.   The $B$ value in benzene is about 30 per cent higher than in cyclohexene.

For the complete thermodynamic characterization of the solution system rubber-cyclohexene the heats of dilution and the entropies of dilution were finally calculated from the temperature dependence of $\Delta\mu_1$ according to Equa-tions (12) and (13).   They have been tabulated in Table VII with reference to 17° C.   The two last columns show that the two quantities (when the inaccu-rate values for $c = 1.1$ are omitted) are proportional to $c^2$ within the limits of error.   The system shows itself to be fairly strongly endothermic.   Notwith-standing this, cyclohexene can be considered a good solvent for rubber due to its high $B$ value.   The dissolving capacity is caused by the high supplementary entropy.

### TABLE VII

#### THERMODYNAMIC DATA REFERRED TO 17° C

| $c \cdot 10^3$ [g. cm.$^{-3}$] | $\Delta\mu_1$, found | $\dfrac{\Delta h_1}{}$ Equation (13) [$\cdot 10^4$ cal mole$^{-1}$] | $T\Delta s_1$ Equation (12) | $\dfrac{\Delta h_1}{c^2}$ [cal mole$^{-1}$ cm.$^6$ g.$^{-2}$] | $\dfrac{T\Delta s_1^E}{c^2}$ [cal mole$^{-1}$ cm.$^6$ g.$^{-2}$] |
|---|---|---|---|---|---|
| 1.1 | −0.86 | +0.64 | + 1.0 | + (53) | + (83) |
| 2.2 | −2.35 | +0.80 | + 2.2 | + 17 | + 46 |
| 3.18 | −4.32 | +3.6 | + 6.6 | + 36 | + 66 |
| 4.21 | −7.29 | +4.8 | +10.7 | + 27 | + 60 |
| Average values: | | | | + 27 | + 57 |

The thermodynamic data can also be calculated from the temperature de-pendence of the 2nd virial coefficient by Equations (9a) and (9b).   This gives the following values:

$$B(7°) = 11.7 \ [\text{Atm. cm.}^6\text{g.}^{-2}]$$

$$B(27°) = 12.7 \ [\text{Atm. cm.}^6\text{g.}^{-2}]$$

$$\Delta B/\Delta T = 0.05 \ [\text{Atm. cm.}^6\text{g.}^{-2}\text{degree}^{-1}]$$

$$\frac{\Delta h_1}{c^2} = 24 \ [\text{cal mole}^{-1} \text{ cm.}^6\text{g.}^{-2}]$$

$$\frac{T\Delta s_1^E}{c^2} = 54 \ [\text{cal mole}^{-1} \text{ cm.}^6\text{g.}^{-2}]$$

A comparison with Table VII shows that herewith, as was to be expected, the same result is obtained as in the numerical evaluation, except that for the latter a better check of the error spread is possible.

### DISCUSSION OF THE EXPERIMENTAL RESULTS

For the discussion of our experimental results we use as a basis the following tabulated results measured at 17° C:

$$M_w = 1.3 \cdot 10^6$$

$$P_w = 19000$$

$$h_{st} = 1750 \text{ Å}$$

$$B = + 12.2 \text{ [atm. cm.}^6\text{g.}^{-2}] = 12.0 \cdot 10^6 \text{ [ergs cm.}^3 \text{ g.}^{-2}]$$

$$B_H = - 10.0 \text{ [atm. cm.}^6\text{g.}^{-2}]; \quad \Delta h_1/c^2 = + 24 \text{ [cal mole}^{-1}\text{ cm.}^6\text{g.}^{-2}]$$

$$B_S = + 22.2 \text{ [atm. cm.}^6\text{g.}^{-2}]; \quad T\Delta s_1{}^E/c^2 = + 54 \text{ [cal mole}^{-1}\text{ cm.}^6\text{g.}^{-2}]$$

When one wants to compare the coil dimensions of rubber with those of other high polymers it is necessary to look at the thermodynamics of its solution to see whether it shows peculiarities. First the high entropy of dilution is remarkable. However, the latter is generally high when the heat of dilution is positive (endothermic). One can segregate the 2nd virial coefficient $B$ according to the equations

$$B_H = B \frac{\Delta h_1}{-\Delta \mu_1{}^E} \quad \text{and} \quad B_S = B \frac{T\Delta s_1{}^E}{\Delta \mu_1{}^E}$$

so that

$$B = B_H + B_S$$

These values are present in the above summary. When $B_S$ is plotted against $B_H$[21,22] for polymethacrylate in various solvents, one obtains the multiplicity of points shown in Figure 10 which indeed does not constitute unequivocal functions but nevertheless does not show a very wide spread in which
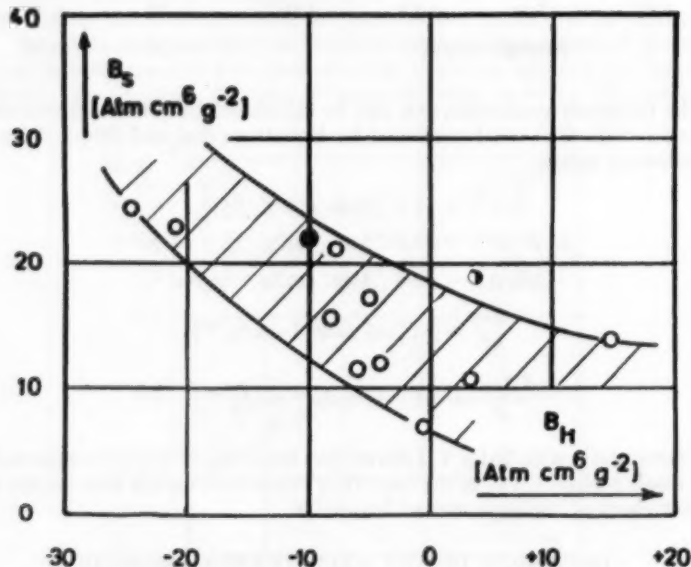


Fig. 10.—Comparison of the $B_H$ and the $B_S$ values for rubber with those for polymethacrylate. ○ Polymethacrylate in various solvents at 31°; ● Rubber in cyclohexene at 17°, our measurement; ◑ Rubber in toluene at 30°, osmotic measurement of Meyer, Wulff, and Boissonas[25].

all the points measured lie.    The values plotted for rubber lie practically within this spread, an indication to the fact that, in its thermodynamic behavior, rubber is comparable with polymethacrylate.    A comparison with this polymer is particularly fitting, notwithstanding the difference in structure since it consists of practically unbranched molecules[23,24].

According to Wahl[25] an unbranched polyisoprene chain of polymerization degree $P$, assuming free rotation and the tetrahedric valence angle, has an end to end distance of

$$h_{st0} = P^{\frac{1}{2}} \cdot 4.02 \cdot 10^{-8} \text{ cm.}$$

If we substitute in it the above value, 553 Å is obtained.    In the same way as in other polymers we find also for rubber experimentally the substantially higher value $h_{st} = 1750$ Å.    The ratio of the two data $h_{st}/h_{st0}$ is 3.16.

We shall try to compare rubber with polymethacrylate also from this point of view.    Cantow and Bodmann[27] determined the coil dimensions of a preparation of this polymer with almost the same molecular weight of our rubber ($M = 1.25 \times 10$), in a series of solvents.    As the authors showed, $h_{st}$ is a function of the $B$ value of the solvent; for $B = 12.2$, $h_{st} = 1420$ accordingly.    For a paraffin chain with free rotation one obtains according to Eyring

$$h_{st0} = 6\sqrt{2n}$$

in which $n$ is the number of $C$ atoms in the chain and $b$ their distance, 1.54 Å, apart.    The polymethacrylate chain used for the comparison contains 25,000 C atoms.    Thus $h_{st0}$ 346 Å and $h_{st}/h_{st0} = 4.1$.    If one uses for comparison a polymethacrylate with the same $h_{st0}$ value as rubber, a higher molecular weight by a factor of $(553/346)^2 = 2.6$ fold must be used.    As the end to end distance increases by a power of slightly greater than 2 of the molecular weight (Cantow and Schulz, Z. physik. Chem. **NF 2**, 117 (1954)) the comparison value of $h_{st}/h_{st0}$ is increased thereby a little, about 5–10%; one would thus have about 4.5.

The rubber molecule is therefore about 23 per cent more tightly coiled than a comparable polymethacrylate molecule under corresponding conditions.    At least a considerable part of this effect can be traced to the fact that the polymethacrylate chain does not have completely free rotation due to the voluminous side groups.

As G. Meyerhoff showed recently[28], in the rotation about the valence angle about $\frac{1}{2}$ of the arc is blocked so that each carbon atom practically can only move freely within $\pm90°$ about the trans direction.    Through this an appreciable stretching of the polymethacrylate molecule occurs, for which there is no correspondence in natural rubber which for four chain atoms has only one methyl group.    Taking this into account we can draw with some caution the conclusion that the rubber molecule is only weakly branched or not at all.

Polyisobutylene is better suited than polymethacrylate for a comparison with rubber.    Its chain is less hindered and more similar to rubber for this reason.    According to measurement by Kunst[29] one may assign to the fraction of $M = 1.2 \times 10^6$, a $B$ value of $12.4 \times 10^{-6}$ ergs cm.$^3$g.$^{-1}$, the end to end distance 1600 Å.    As per Eyring's formula the calculated end to end distance is $h_{st0} = 460$ Å.    As is to be expected the ratio $h_{st}/h_{st0} = 3.6$ lies between that of rubber and that of polymethacrylate.    Since polyisobutylene is produced ionically it is almost completely unbranched.    The comparison with these polymers points, therefore, even more strongly to only a slight branching of rubber.

As already mentioned, we have communicated in this paper a series of results which have a somewhat provisional character. The investigation is now being extended to fractionated rubbers and in addition also other solvents will be drawn upon, in order to obtain a more profound view into the thermodynamic-statistical behavior of rubber.

## ACKNOWLEDGMENTS

## SUMMARY

An experimental method of preparing and purifying natural rubber solutions in the absence of oxygen with an ultracentrifuge is presented. The solutions are suitable for optical measurements. Light scattering is measured as a function of concentration, angle, wave length and temperature. By determining molecular weight, diameter of the coiled molecule, and thermodynamic quantities ($\Delta\mu_1$, $\Delta h_1$, $\Delta s_1$) in this way it is possible to get information on branching of the rubber molecules.

The method was used for cyclohexene solutions of a carefully tapped crepe rubber. The molecular weight was $1.3 \cdot 10^6$ and the end to end distance of the coil 1750 Å. The heat of dilution was positive (endothermic) the $B$-value being nearly as high as that found in benzene solution by osmotic measurements. Comparing these results with measurements on unbranched polymethacrylate and polyisobutylene one can conclude that these rubber molecules are not or only slightly branched.

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# SHEAR DEPENDENCE OF VISCOSITY OF
# NATURAL RUBBER SOLUTIONS *

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In an earlier paper[1] viscosity measurements on dilute Alfin polyisoprene solutions at quite low shear rates were reported. It was shown that the limiting slope of the intrinsic viscosity vs. rate of shear plot at low shear rates, $(\Delta[\eta]/\Delta D)_{D \to 0}$, is proportional to the square of the zero shear intrinsic viscosity $[\eta]_0^2$. This relationship suggested the possibility of using the slope of the $(\Delta[\eta]/\Delta D)_{D \to 0}$ vs. $[\eta]_0^2$ plot as a molecular weight-independent parameter expressing the magnitude of the shear dependence of intrinsic viscosity, and thus as a possible means for studying polymer microstructure. It was thought that polymers having different structures would give rise to linear plots of the latter type, but with different slopes. To test this view, it was deemed desirable to extend viscosity measurements to another polyisoprene system, namely, natural rubber. This note describes the results obtained from viscosity measurements on Hevea fractions, and shows the comparative shear effects for both the natural *cis* and the predominantly *trans* Alfin polyisoprenes.

## EXPERIMENTAL

The Hevea was a sample of pale crepe. The polymer was dissolved in benzene and the gel fraction extracted by filtration through a fine wire screen. The soluble portion was then fractionated by the usual precipitation of polymer from benzene solution with methanol. The six highest fractions, varying in molecular weight from about one to four million (Table I), were employed. The natural rubber solutions were stabilized by incorporation of tetramethylthiuram disulfide to the extent of 1 per cent on the polymer. Viscosity measurements were carried out on benzene solutions of polymer fractions at $25 \pm 0.01°$ C over the approximate shear range of 100 to 600 sec.$^{-1}$ in the horizontal capillary viscometer previously described[1], following the same procedure as before.

## TABLE I

### MOLECULAR WEIGHTS OF HEVEA FRACTIONS

| Fraction | $[\eta]_0$ | Mol. wt. $\times 10^{-6}$ |
|---|---|---|
| A | 14.0 | 3.87 |
| B | 12.1 | 3.12 |
| C | 10.8 | 2.70 |
| D | 9.2 | 2.25 |
| E | 8.4 | 1.95 |
| F | 5.8 | 1.07 |
| U (Unfractd.) | 8.8 | 2.10 |

## RESULTS AND DISCUSSION

Experimental curves of reduced viscosity vs. rate of shear were obtained for three concentrations of each of the various fractions, as well as for the unfractionated polymer. Typical plots are shown in Figure 1. From such graphs, isoshear plots of $\eta_{sp}/c$ vs. $c$ at various gradients were constructed, and these in turn were extrapolated to zero concentration to give intrinsic viscosity at various rates of shear over the range considered. Figure 2 shows the shear dependence of intrinsic viscosity for the various Hevea fractions. The slopes of these lines were then plotted against the squares of the zero shear intrinsic viscosities, as shown in Figure 3, where they are seen to fall along the straight line obtained previously for Alfin polyisoprene[1]. Now, the all-cis-1,4-polyisoprene structure of Hevea contrasts with the very high trans-1,4-structure of the Alfin polymer which also contains substantial pendant vinyl and isopropenyl groups[2]. Thus, in spite of the known structural differences between the two polyisoprenes, the non-Newtonian behavior of their dilute solutions as represented by the suggested molecular weight-independent parameter is virtually the same.

There is, however, one interesting qualitative difference between the shear effects for the two polymers. The slopes of the lines in Figure 1 are all greater than corresponding ones for the Alfin polymers of roughly the same molecular weight and solution concentration. (Compare Figure 1 of the present paper with Figure 2 of Reference 1). This may be seen from Table II, although, fortuitously, no strictly comparable results are available. Nevertheless, it is evident that Hevea fraction B, with a somewhat smaller estimated molecular weight than Alfin 1c, has a much larger viscosity-shear slope than does the latter,
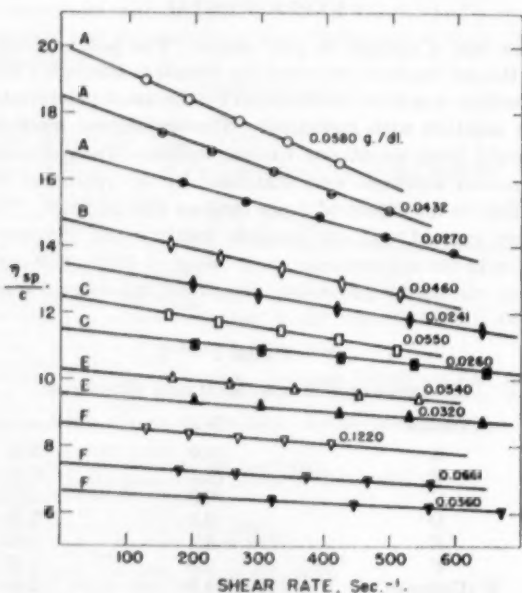


FIG. 1.—Reduced viscosity versus rate of shear for Hevea fractions of different molecular weight in benzene at 25° C.
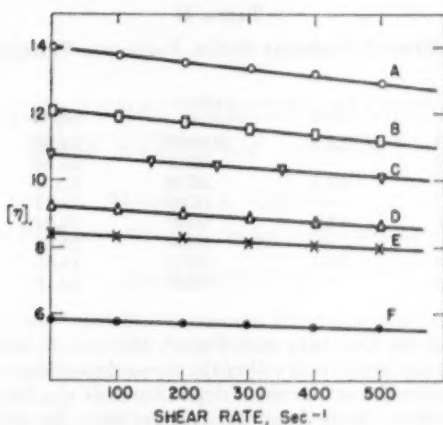
Fig. 2.—Shear dependence of intrinsic viscosity for various Hevea fractions in benzene.

at more or less the same concentrations; similarly for Hevea fraction C and Alfin 3a. Unfortunately, these results cannot be conveniently reduced to any common denominator for comparison short of the molecular weight-independent parameter already mentioned. This, of course, has been shown to be insensitive to the structural differences between the two samples of polyisoprene under consideration.
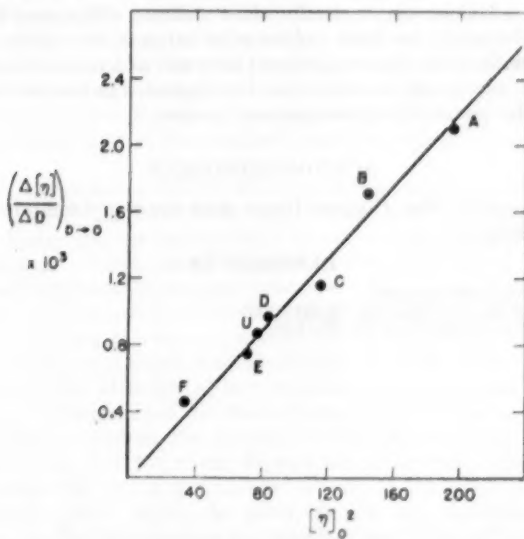


Fig. 3.—The limiting slope of the intrinsic viscosity-rate of shear curve plotted against the square of the zero shear intrinsic viscosity. The circles correspond to present data for Hevea fractions and the line represents the relation obtained previously for Alfin polyisoprene.

## TABLE II

#### SLOPES OF TYPICAL VISCOSITY–SHEAR PLOTS FOR VARIOUS POLYMERS

| Fraction | $[\eta]_s$ | Concn. g./dl. | $(\eta sp/c)_s$ | $-\left(\dfrac{\Delta \eta sp/c}{\Delta D}\right) \times 10^s$ |
|---|---|---|---|---|
| Hevea—B | 12.1 | 0.0460 | 14.80 | 4.20 |
| B | — | .0241 | 13.50 | 3.00 |
| C | 10.8 | .0550 | 12.55 | 3.24 |
| C | — | .0260 | 11.47 | 1.84 |
| Alfin—1c | 12.8 | .0500 | 16.24 | 2.86 |
| 1c | — | .0250 | 14.62 | 2.24 |
| 3c | 10.3 | .0595 | 14.00 | 2.68 |
| 3a | — | .0298 | 12.10 | 1.64 |

As pointed out by Goldberg and Fuoss[3], the non-Newtonian behavior of polymer solutions can arise from either the shear dependence of interaction between polymer molecules or the shear dependence of the intrinsic viscosity, or both. Since the latter factor is apparently the same for the two polymers in question, it follows that the remaining difference between them must be ascribed to the difference in the shear dependence of polymer interaction. Now, examination of the isoshear plots of Alfin polyisoprene[1] reveals that the Huggins $k'$ is more or less contant over the shear range 0–600 sec.$^{-1}$ (e.g., 0.36 for fraction 1a), whereas with the natural rubber molecule $k'$ decreases with shear rate (e.g., from $k' = 0.41$ at $D = 0$ to $k' = 0.25$ at 600 sec.$^{-1}$ for Hevea fraction B). The explanation for this disparity in the shear dependence of interaction is presently unknown.

It appears from the above that the shear effect in dilute solutions may not be used readily for studying microstructural differences in polymers, although concentrated solutions may actually show definite differences between such polymers. Moreover, for most polymers of interest, the dilute solution viscosities are smaller than those considered here and as a result their shear effects are much less pronounced, in which case the suggested parameter would be even less likely to be useful for microstructural studies.

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# VISCOSITY OF NATURAL RUBBER SOLUTIONS AT VERY LOW RATES OF SHEAR *

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## INTRODUCTION

In a previous paper[1] describing reduced viscosity measurements on Alfin polyisoprene over the fairly wide range of shear rates 100–20,000 sec.$^{-1}$, it was shown that a theoretical relation proposed by Bueche[2] to account for the non-Newtonian flow of high polymer solutions fitted the experimental data rather well, at least up to about 12,000 sec.$^{-1}$. Beyond this point, the Bueche plot fell steadily below the experimental points. Inasmuch as his theoretical expression was derived by dropping terms which become important only at large shear rates, it appeared that the Bueche equation, when modified to incorporate some of these terms, would fit the over-all data quite well even up to about 20,000 sec.$^{-1}$. At the same time, the revised equation would have to take into consideration the ultimate asymptotic levelling-off of the reduced viscosity at very high gradients.

As recommended by Bueche and indicated in the earlier paper, there is a definite need to obtain further data at shear rates well below 100 sec.$^{-1}$ in order to ascertain the reliability of the Bueche relation in the very low shear range. Since the gradient enters to the one-half power in the equation at low shear rates, this relation implies a virtually infinite slope of the reduced viscosity-shear curve at the ordinate. Previous work[1], however, over the range 100–500 sec.$^{-1}$ showed the reduced viscosity to increase in an approximately linear fashion with decrease in rate of shear. Consequently, the exact shape of the reduced viscosity-shear plot at the smallest possible gradients deserves renewed attention.

Chang and Morawetz[3] have recently described a procedure for determining the shear dependence of viscosity at very low rates of shear. This involves following the change of pressure head with time of a liquid flowing in a capillary U-tube viscometer. Curvature in the plots of the logarithm of pressure head versus time indicates non-Newtonian behavior. By means of this procedure, measurements could be readily extended down to shear rates somewhat below 1 sec.$^{-1}$. This is about the lower practical limit of shear rate attainable in a capillary viscometer for a liquid with a viscosity of about 10 to 20 centipoises.

In connection with attempts at investigating microstructural differences in polymers through differences of the shear effects, recent attention in these laboratories has been focused on the natural rubber molecule. It has been observed, for example, that the shear dependence of intrinsic viscosity for the polyisoprene molecule—be it the natural all-*cis*, or the predominantly *trans* Alfin polymer—is pretty much the same for the two substances[4]. For an examination of the Bueche equation at very small gradients, natural rubber was consequently selected for study. This paper reports the results obtained from

reduced viscosity measurements on Hevea solutions at rates of shear from about 500 down to less than 1 sec.$^{-1}$, using the method of Chang and Morawetz.

## EXPERIMENTAL

Two U-tube viscometers were used in this work, one covering the shear range 100 down to less than 1 sec.$^{-1}$ (MV-2), the other covering the wider range 0–500 sec.$^{-1}$ (MV-4). Each arm of the former viscometer contains a 25 cm. length of precision bore capillary (radius 0.025 cm.) for a total capillary length of 50 cm. A 14 cm. length of precision bore capillary (radius 0.020 cm.) is contained in each arm of the latter viscometer. These instruments are essentially continuously varying pressure head viscometers. Identical cylindrical working volumes in the two arms of each viscometer are assured by the use of precision bore tubing above the capillaries (0.6 cm. I.D.; height 20 cm. in MV-2, 31 cm. in MV-4). To avoid having a curved capillary in the U tubes, the arms are joined at the bottom by a piece of tubing of about 6 mm. inside diameter. The over-all heights of both viscometers are about 47 cm. They were firmly supported in a vertical position in a constant temperature bath set at $25\pm0.01°$ C. The bath was an aquarium type with plate glass sides suitable for viewing the menisci with a cathetometer.

The procedure involved first adjusting the liquid levels above the capillaries so that a driving pressure of about 3–5 cm. of benzene in MV-2, or about 13–16 cm. in MV-4, was established. Then measurements were made of the levels in the viscometer arms at various time intervals, as the liquid flowed through the capillary under its own weight, until the driving pressure fell to about 2 or 3 mm. From the definition of viscosity $\eta$, it may be seen that for Newtonian flow

$$\ln h/h_0 = - (gR^4d/4a^2\eta l)t = St \tag{1}$$

where $h$ and $h_0$ are the actual differences in liquid levels at time $t$ and at the outset of a run respectively, $d$ is the density of the liquid, $R$ and $l$ are the capillary radius and length, $a$ is the radius of the cylindrical working volume, and $g$ is the gravitational constant. Figure 1 shows the linear plots of log $h/h_0$ vs. $t$ for a Newtonian liquid, such as benzene, in the low shear viscometers. The good agreement between the measured slopes of the lines based on the corresponding natural logarithm plots, $(-3.20 \times 10^{-3}$ and $-2.32 \times 10^{-3}$ sec.$^{-1}$ for MV-2 and MV-4, respectively) and the corresponding values of $S$ calculated from the approximate instrumental dimensions and known constants of benzene ($-3.08 \times 10^{-3}$ and $-2.25 \times 10^{-3}$ sec.$^{-1}$) using Equation (1) is evidence for the reliability of this approach. Obviously this procedure could serve as an absolute method for determining the viscosity of a Newtonian liquid.

Curvature in the log $h/h_0$ vs. $t$ plot indicates non-Newtonian behavior. If $S$ is the slope of such a plot for a solution at some particular value of $h$, and $S_0$ the slope for the solvent, then the relative viscosity of the solution at the rate of shear corresponding to the given head is simply $S_0/S$. By drawing tangents at a number of points in each of the experimental curves and evaluating $S_0/S$ for the respective gradients, reduced viscosity data over the range of shear rates mentioned above for the two viscometers were readily derived for the various natural rubber solutions.

No kinetic energy corrections were applied to the flow data in this work since these were considered negligible under the given experimental conditions.
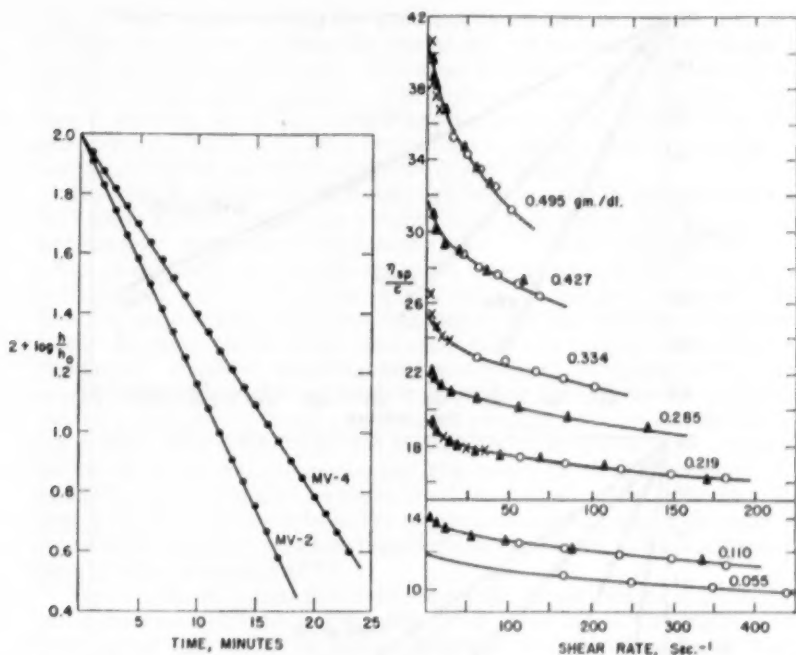
FIG. 1.—Plots of log $h/h_0$ vs. time for a Newtonian liquid (benzene) in the two low shear viscometers.

FIG. 2.—Effect of rate of shear on the reduced viscosity of natural rubber in benzene at 25° C. The various points were obtained with the five-bulb viscometer (○), and U-tube viscometers MV-2 (×) and MV-4 (▲), respectively. The lines were derived from the Bueche equation.

Mock and Marshall[5] have recently discussed the kinetic energy correction for this type of viscometer.

As a further check on the reliability of the data obtained by the above method, viscosity measurements over the range 100–500 sec.[-1] were also made with a five-bulb viscometer of the Krigbaum-Flory type. The procedure followed with this viscometer has been described before[i].

The maximum rate of shear, $D$, at the wall was calculated by means of the relation

$$D = Rghd/2\eta l \qquad (2)$$

The natural rubber was a sample of pale crepe, having a viscosity average molecular weight of about 2,100,000. Viscosity measurements were carried out on gel-free benzene solutions varying in concentration from about 0.05 to 0.5 g./dl. The rubber solutions contained tetramethylthiuram disulfide to the extent of 1 per cent on polymer for stabilization.

## RESULTS AND DISCUSSION

Typical flow data for various concentrations of natural rubber in benzene, obtained in the MV-2 viscometer, are shown as the points joined by the solid lines in Figure 3. The dotted lines are tangents to the curves at the onset of
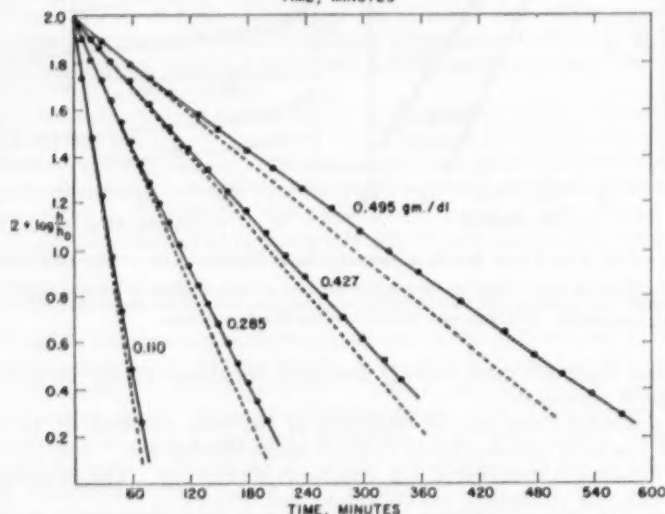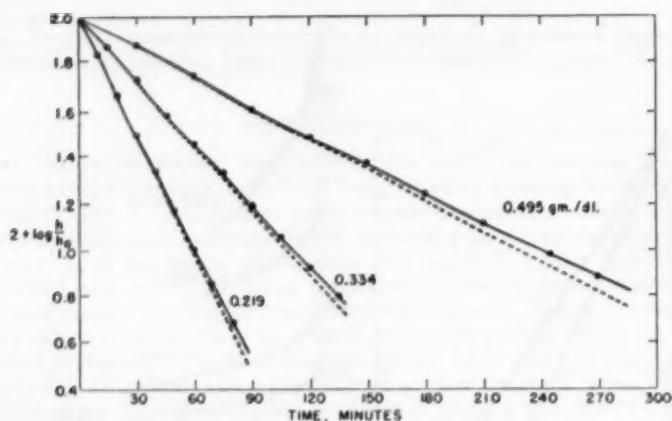
FIG. 3.—Plots of log $h/h_0$ vs. time for three non-Newtonian solutions (natural rubber in benzene) in viscometer MV-2.

FIG. 4.—Plots of log $h/h_0$ vs. time for four non-Newtonian solutions (natural rubber in benzene) in viscometer MV-4.

flow in the U-tube viscometer. The slopes of these tangents, $S$, divided by that for benzene, $S_0$, give the relative viscosities for the several solutions corresponding to the initial hydrostatic heads (and hence mean shear gradients). These solutions were also run in the five-bulb viscometer (see Figure 2) in which the lowest rate of shear was higher than the highest in the MV-2 viscometer. Significantly, the initial reduced viscosity values, $\eta_{sp}/c$, obtained in the latter instrument as described above are all larger than corresponding values obtained in the five-bulb viscometer, and moreover are approximately the values which would be predicted by extrapolation of the nearly linear plots of the five-bulb

data.  Now, in determining the remaining viscosity-shear points with MV-2, tangents were drawn to the solid lines at various places and their slopes were used to calculate $\eta_{sp}/c$ values.  The mean gradients were calculated from the heads at the points of tangency.  The method of arriving at the shear depend- ence of viscosity using the Chang-Morawetz approach is illustrated by the re- sults presented in Table I for a typical run in the low shear viscometer.  Fi- nally, $\eta_{sp}/c$ values were plotted against $D$ as in Figure 2.

It should be pointed out that although the curvature in the various $\log h/h_0$ vs. $t$ plots appears slight, the reduced viscosities are nevertheless changing quite rapidly with drop in hydrostatic head.  This curvature, of course, be- comes progressively less pronounced as the concentration of the rubber solution is diminished.  For a concentration of 0.055 g./dl. the plot is so nearly linear that it is quite hazardous to draw tangents to the line, and hence this was not done.  However the five-bulb data show that this solution is likewise non- Newtonian.  Since the experimental technique is quite simple and inherently capable of a high degree of accuracy, each point in the $\log h/h_0$ vs. $t$ plot must be treated as fully accurate and a smooth line permitted to pass through the vari- ous points.  The difficulty in this method lies in having to draw tangents to the curves at the various points, and this results in some uncertainty in the particular value calculated for the reduced viscosity at a given gradient.  How- ever, there is no uncertainty in the trend of sharply increasing viscosity with reduction in rate of shear, which behavior is in accord with some recent observa- tions of other investigators[6,7,8].

Figure 4 shows typical flow data for several concentrations of natural rub- ber in benzene obtained in the wider shear range MV-4 viscometer.  From these curves $\eta_{sp}/c$ values at various gradients were calculated in the manner outlined above and plotted in Figure 2, where they are seen to overlap data obtained with both the MV-2 and five-bulb viscometers.  This overlapping strengthens our confidence in the reliability of these results.

An attempt to fit the composite data to the Bueche equation is indicated by the solid lines in Figure 2.  As is clearly seen the agreement is very good. Since this equation was previously shown[1] to represent the reduced viscosity data rather well over the very wide range of 100 to 12,000–20,000 sec.$^{-1}$, the present work has provided therefore experimental confirmation of the correct-

TABLE I

DETERMINATION OF VISCOSITY–SHEAR RELATION FOR NATURAL RUBBER IN BENZENE AT 25° C IN MV-2 VISCOMETER*

| $t$, min. | $h$, cm. | $h/h_0$ | $2+\log h/h_0$ | $S$, sec.$^{-1}\times10^4$† | $\eta$ | $\eta_{sp}/c$ | $D$, sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0 | 4.850 | 1.000 | 2.000 | — | — | — | — |
| 30 | 3.600 | 0.742 | 1.870 | −1.670 | 19.20 | 36.8 | 6.4 |
| 60 | 2.675 | 0.552 | 1.742 | — | — | — | — |
| 90 | 2.000 | 0.412 | 1.615 | −1.637 | 19.58 | 37.5 | 3.5 |
| 120 | 1.490 | 0.307 | 1.487 | — | — | — | — |
| 150 | 1.125 | 0.232 | 1.365 | −1.611 | 19.90 | 38.2 | 1.9 |
| 180 | 0.844 | 0.174 | 1.240 | — | — | — | — |
| 210 | 0.640 | 0.132 | 1.120 | — | — | — | — |
| 245 | 0.465 | 0.0959 | 0.982 | — | — | — | — |
| 270 | 0.375 | 0.0773 | 0.888 | −1.520 | 21.10 | 40.6 | 0.6 |
| 300 | 0.289 | 0.0595 | 0.775 | — | — | — | — |

* Conc. 0.495 g./dl.
† $S_0$ (benzene) $= -3.204 \times 10^{-4}$ sec.$^{-1}$.

<div align="center">

TABLE II

SUITABILITY OF BUECHE EQUATION FOR EXPRESSING SHEAR
DEPENDENCE OF VISCOSITY

Data of natural rubber in benzene, conc. 0.427 g./dl., at 25° C

</div>

| $D$, sec.$^{-1}$ | $\eta_{sp}/c$, exptl. | $\eta_{sp}/c$, calc.* |
|---|---|---|
| 1 | 31.3 | 31.2 |
| 5 | 30.0 | 30.3 |
| 10 | 29.4 | 29.7 |
| 20 | 28.8 | 28.8 |
| 30 | 28.3 | 28.1 |
| 40 | 27.7 | 27.6 |
| 50 | 27.2 | 27.0 |
| 60 | 26.7 | 26.6 |
| 70 | 26.2 | 26.2 |

* Calculated assuming $k = 4.2 \times 10^{-4}$ and $(\eta_{sp}/c)_0 = 32.0$.

ness of this formula down to extremely small rates of shear. Moreover, it has furnished a nice technique for evaluating the zero shear reduced viscosity without the necessity of performing an uncertain extrapolation. Essentially, it requires the determination of the parameters of the Bueche formula, which best satisfies the experimental data over a fairly wide range of shear rates. Calculation of the zero shear reduced viscosity from such a derived expression is then immediately possible. An example will illustrate this point. For our purposes, the Bueche equation may be expressed simply as

$$\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_0 \left[1 - k\left(\frac{\eta_{sp}}{c}\cdot D\right)^i\right] \tag{3}$$

where $\eta_{sp}/c$ and $(\eta_{sp}/c)_0$ are the reduced viscosities at shear rates $D$ and zero, respectively, and $k$ is a constant embracing a number of molecular parameters. Several experimental values of $\eta_{sp}/c$ and $D$ are substituted into the relation to give an average value of $k$, and also an approximate value for $(\eta_{sp}/c)_0$. Using these values for $k$ and $(\eta_{sp}/c)_0$, a set of reduced viscosities are then calculated for the different gradients, and compared with the experimental viscosities. These values for $k$ and $(\eta_{sp}/c)_0$ are then varied somewhat and the process repeated until as good a fit as possible of the equation to the data can be found. The value for $(\eta_{sp}/c)_0$ which makes the Bueche equation fit the data best may then be considered as the true zero shear reduced viscosity. Although this point may be open to question, in the absence of any other method for uniquely determining the zero shear reduced viscosity, it is the author's view that the present approach should be adopted as a regular method for obtaining $(\eta_{sp}/c)_0$. This has the obvious advantage of avoiding an unreliable extrapolation in a gradient range where the viscosity is very shear dependent. Typical results obtained by this method are shown in Table II, where the calculated and experimental values for $\eta_{sp}/c$ are indeed in close agreement. Although this work emphasized the Chang-Morawetz procedure, it is not essential to use it in order to arrive at a reasonable value for $(\eta_{sp}/c)_0$. Actually the data from the five-bulb viscometer are sufficient for this purpose, since in all cases the Bueche plot passes through these experimental points, and hence the zero shear reduced viscosity can be recovered from such viscosity-shear data in the manner outlined above.

## SUMMARY

The shear dependence of viscosity of benzene solutions of natural rubber was studied at rates of shear from about 500 down to less than 1 sec.$^{-1}$. Measurements involved following the change of pressure head with time of the various solutions flowing in a capillary, U-tube viscometer. Curvature in the plots of the logarithm of pressure head versus time indicated non-Newtonian flow. From such curves, reduced viscosity data over the above-mentioned shear range were readily derived. As a check, data over the range 100–500 sec.$^{-1}$ were also obtained with a five-bulb viscometer of the Krigbaum-Flory type, and these data overlapped those obtained with the U tube. The reduced viscosity increased very sharply with decrease in gradient, making extrapolation to the viscosity axis quite unreliable. However, a theoretical relation proposed by Bueche fitted the composite data rather well. This work furnished a nice technique for determining the zero shear reduced viscosity $(\eta_{sp}/c)_0$ without the necessity of performing an uncertain extrapolation: evaluate the parameters of the Bueche formula which best satisfies the experimental data over a fairly wide range of shear rates, and then calculate $(\eta_{sp}/c)_0$ directly.

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# INTERACTION OF RUBBER AND
# CARBON TETRACHLORIDE*

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Carbon tetrachloride has been used for studies on the solution properties of natural rubber. It has been tacitly assumed that no chemical reaction between the two takes place; but carbon tetrachloride has been found to show a negative heat of mixing with natural rubber. There is absorption of heat (0.37–1.36 cal./g.) with benzene, dichloroethylene and toluene, while there is evolution of heat (2–3 cal./g.) with carbon tetrachloride and chloroform[1]. There is considerable evolution of heat[2] on mixing cellulose triacetate with tetrachloroethane and the solvent is found to be completely bound with the polymer. It appears therefore that similar combination between rubber and carbon tetrachloride may occur, when these are brought together. An indication of chemical interaction of carbon tetrachloride and rubber has been found in an examination of the spectra of carbon tetrachloride solutions of natural rubber[3]. Chemical analysis of rubber, aged in solution at the laboratory temperature, showed that chlorine was incorporated into the rubber.

In the present investigation a progressive detailed study of the system of deproteinized rubber-carbon tetrachloride has been carried out from the instant the two are brought in contact till either a homogeneous solution (in darkness only) or a gel is obtained (visible radiations).

## EXPERIMENTAL

Deproteinized natural rubber (about 0.2 g.) was accurately weighed. An amount of $CCl_4$ that would furnish a 2 per cent (w/v) solution was taken in a pyrex tube (20 cc.) having a ground-glass joint. The weighed rubber was added under the conditions of experiment and the tube closed with another pyrex tube (20 cc.) with a reciprocal ground-glass joint. The opposite end of this second tube had earlier been drawn out into a capillary and sealed. For the experiments with diffused daylight and direct sunlight, the tubes were exposed on racks. In experiments with different wavelengths of light, the tubes were mounted on a water-cooled panel opposite 'Baker' $2'' \times 2''$ filters and placed about $10''$ away and equidistant from a 200 watt clear tungsten lamp. Experiments were also carried out in which samples were mixed and kept in complete darkness.

After the exposure, the capillary was broken under water, which caused water to rush into the tube. The contents of the tubes were refluxed for fifteen minutes and the hydrogen chloride determined. The chlorine content of the rubber left from refluxing was determined after precipitation with methyl alcohol, followed by solution in benzene and reprecipitation with methyl alcohol.

## DISCUSSION

It is observed (Table I) that evolution of HCl progressively increases and attains a value of 7 per cent in 1980 hours of exposure in direct sunlight; exposure to diffused daylight also gives off HCl which attains a value of 1.2 per cent in 108 hours.   There is a simultaneous incorporation of chlorine as well.   It has been found possible to attain as high a chlorine content at 31 per cent on prolonged exposure to sunlight.

Table II shows that hydrogen chloride is evolved when the samples are exposed to radiations of wavelengths about and below 5200 Å, chlorination of rubber also taking place simultaneously.   Such reactions also take place when rubber —CCl$_4$ systems are exposed in a quartz tube to U.V. radiation (3600 Å).

In samples which were mixed and kept in complete darkness there was no hydrogen chloride evolution.

These results show that CCl$_4$—rubber systems progressively pass on into partially chlorinated rubber —CCl$_4$ systems, with evolution of HCl unless they are kept in complete darkness or exposed only to light of wavelengths above 5200 Å.

This observation throws doubt on the validity of the results of solution properties of rubber—CCl$_4$ systems, reported in literature, since a part of the rubber would have changed into chlorinated rubber.   Hock and Schmidt[1] observed a negative heat of solution when rubber was dissolved in CCl$_4$.   The evolution of HCl during this dissolution process explains this negative heat of solution.

Kharasch, Jensen, and Urry[4] have shown that mono-olefins, such as octene-1, react with CCl$_4$ only in presence of peroxides or ultraviolet light, these being responsible for the splitting of CCl$_4$ into radicals.   They do not report the evolution of HCl by a substitutive attack of the free radicals on the olefin. The absence of a chemical reaction between rubber and CCl$_4$ in the dark suggests that peroxidic centers, even if present in unmasticated deproteinized rubber, are not responsible for this reaction.   Bateman[5] has shown that photodecomposition of natural rubber takes place only when rubber is irradiated with ultraviolet light.   That photodissociation of CCl$_4$ does not take place with visible radiation can be judged from the fact that its absorption continuum[6] has been reported to be in the ultraviolet region (2800 Å to 2700 Å). The fact that hydrogen chloride is evolved under conditions, which normally exclude the decomposition of either rubber or CCl$_4$, suggests that rubber-CCl$_4$ systems give rise to hydrogen chloride and chlorinated rubber even at lower energy levels by absorption of light of wavelengths between 3000 Å and 5200 Å. Results in Table II indicate that at energy levels lower than that corresponding to 5200 Å no chemical change takes place, as revealed by the absence of HCl.

### TABLE I

#### DIRECT SUNLIGHT IN PYREX TUBE

| Exposure time in hours | — | 12 | 24 | 48 | 60 | 96 | 168 | 1980 |
|---|---|---|---|---|---|---|---|---|
| Free HCl, wt. % of rubber | — | 0.4 | 1.4 | 1.5 | 2.2 | 2.4 | 3.3 | 7.1 |
| Cl content of the rubber, % | — | 1.5 | 3.3 | 4.3 | 6.7 | — | 9.12 | 31.0 |

#### DIFFUSED DAYLIGHT IN PYREX TUBE

| Exposure time in hours | — | 12 | 24 | 36 | 84 | 108 |
|---|---|---|---|---|---|---|
| Free HCl, wt. % of rubber | — | 0.2 | 0.3 | 0.6 | 0.9 | 1.2 |
| Cl content of rubber, % | — | 1.3 | 1.2 | 2.0 | 2.8 | 3.94 |

TABLE II

| Nature of tube | Time of exposure, hours | Nature of exposure | Free HCl wt. % of rubber | Cl content of the rubber, % |
|---|---|---|---|---|
| Pyrex | 96 | Red filter, 6500 Å | 0.0 | 0.0 |
| Pyrex | 96 | Yellow filter, 5800 Å | 0.0 | 0.0 |
| Pyrex | 96 | Dark green filter, 5200 Å | 0.0096 | 0.0 |
| Pyrex | 96 | Dark blue, 4700 Å | 0.076 | 0.71 |
| Quartz | 15½ | U.V., 3600 Å | 0.69 | 2.5 |
| Quartz | 36 | U.V., 3600 Å | 1.59 | 6.5 |

The following explanations are offered for the observations on the interaction of rubber and CCl₄ even with radiations of longer wavelength.

Transference of high energy through macromolecules has been suggested by Alexander and Charlesby[7] to explain the particular behavior of various polymers under the action of high energy radiation. In the present investigation reactions requiring normally a higher energy, viz., photodecomposition of either rubber or carbon tetrachloride to furnish radicals, are brought about in this macromolecular system by the absorption and transference of lower energies.

From an examination of the infrared spectrum of CCl₄ solutions of natural rubber[3] it has been postulated that a complex is formed between the two. It is also possible that even the low energies corresponding to 5200 Å, absorbed in various parts of the rubber chain, result in the decomposition of the complex to provide radicals, which then chlorinate the rubber and at the same time, to some extent, react substitutively, giving off hydrogen chloride.

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# THE ROLE OF DIFFUSION OF POLYMER CHAINS IN
# THE MECHANISM OF ADHESION AND AUTOHESION
# OF RUBBERS*

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The most characteristic feature of autohesion effects in rubber and other polymers is the increase of the adhesion forces with time of contact. Two mechanisms have been used in the interpretation of the observed kinetics of autohesion: a macroscopic mechanism, involving an increase of the total area of true contact owing to relaxation and plastic flow in the zone of contact stresses[2], and a microscopic (molecular) mechanism of diffusional intertwining of adjacent molecular chains, which leads to increasing adhesion in these regions to a value corresponding to cohesion, owing to the disappearance of the physical boundary of separation[1].

The concept of a diffusion mechanism for the autohesion of rubbers was first advanced by Josefowitz and Mark[1] and subsequently developed by Deryagin and Krotova[2] and Voyutsky and his associates[3].

Since relaxation effects also increase with increasing mobility of the chains and their segments, for both mechanisms the rates of cohesion determined by them should vary in a similar manner with the temperature and the type of polymer. Therefore the investigations on autohesion so far carried out do not make it possible to determine the relative significance of the two mechanisms— the chain-molecular and the relaxation-mechanical. An attempt was made in the present investigation to determine the relative importance of the two mechanisms, with the use of two new ideas.

The first idea consists of the measurement of the adhesion forces between two crossed threads, covered with films of the polymers of different thicknesses, including very low values ($10^{-6}$ cm). If the films are very thin, the role of their deformation and relaxation is slight, the contact area is extremely small, and therefore both mechanisms, the macroscopic and the microscopic, which are presumed to form the basis of autohesion kinetics, should not operate, in contrast to the case of fairly thick films.

The second idea is to investigate by some method or other the adhesion not only of similar polymers (rubbers) but different combinations (pairs) of them, and to compare the adhesion results with compatibility data for the rubbers. This idea was first advanced by us at the conference on adhesion held at the Institute of Physical Chemistry, Academy of Sciences USSR, in May 1955.

Specifically high values of adhesion for definite pairs in parallel with their compatibilities would indicate the role of a molecular, diffusion mechanism in autohesion and adhesion of polymers. Conversely, with a relaxation mechanism adhesion should not be correlated with compatibility.

## AUTOHESION OF RUBBERS

For investigation of the autohesion of films of various thicknesses of different types of rubber by the crossed thread method, use was made of the technique developed by Deryagin and Malkina[4], somewhat modified by Moskvitin and Futran[5]. The quartz threads of the instrument were coated with thin uniform films of the rubbers. The films were applied to the quartz threads from solution by the drain-off method proposed by Deryagin[6]. The threads were immersed in a benzene solution of rubber, which was then drained off at a definite rate. The instrument for application of the films, shown in Figure 1, consists of the following parts: a quartz rod 1, rigidly fixed in a stand, with threads which are coated with the rubber films, a cork float 4, on which a beaker 3 containing the rubber solution is firmly fixed, and a vessel with water 5, rigidly fixed in the stand 9.

The vessel 5 is emptied with the aid of the tube 6, fitted with a micro-tap 7. The turn of the tap in degrees is noted on the scale 8 by means of a pointer attached to the tap. In this way it is possible to set up a required rate of water efflux from the vessel 5, and therefore also the rate of movement of the beaker containing the rubber solution relative to the stationary thread 2. The thickness of the film remaining on the quartz thread depends on the rate of displacement of the beaker with the solution.

Quartz threads 150–200 $\mu$ in diameter were used, i.e., relatively thick threads, as the autohesion forces for rubbers are very high. The threads were drawn before each experiment, to avoid surface contamination.

The drying time of the threads before application of the rubber films was 30 or 60 minutes, according to the thickness of the films.

The thickness $h$ of the polymer layer applied to the thread was calculated with the aid[7] of the formula:

$$h = 1.32 \cdots r \left( \frac{\eta u}{\sigma} \right)^{\frac{1}{2}} c \tag{1}$$

where $h$ is the film thickness in cm.; $r$ is the radius of the thread in cm.; $\eta$ is the solution viscosity in poises; $u$ is the drain-off rate of the rubber solution in cm. /second; $\sigma$ is the surface tension in dynes/cm.; $c$ is the volume concentration of rubber.

The viscosity of the rubber solutions was determined in an Ubbelohde vis-
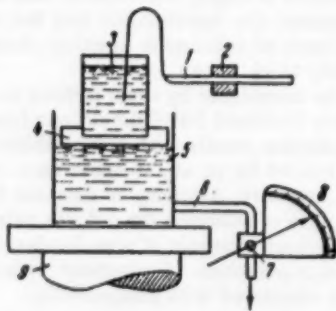


Fig. 1.—Apparatus for application of films of definite thickness to threads by the drain-off method.
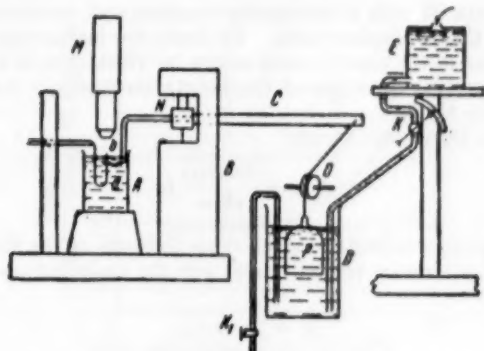
Fig. 2.—Diagram of apparatus for measurement of autohesion forces
by the crossed thread method.

cometer. The viscosity was calculated from the formula

$$\eta = C(P\tau)_{av}$$

where $\eta$ is the viscosity in poises; $P$ is the average efflux pressure in cm. water column; $\tau$ is the efflux time in seconds; $(P\tau)_{av}$ is the arithmetical average of all the determinations; $C$ is the viscometer constant.

Figure 2 shows a diagram of the apparatus used for determinations of autohesion forces. Two freshly drawn quartz threads $\sim150$ $\mu$ in diameter were fixed in the beaker $A$. The thread $a$ was fixed vertically with the thick end held rigidly in a stand; the thread $b$ was fixed horizontally. Thus, the threads met at $90°$. The thread $b$ was fixed in a specially designed stand $B$, the main part of which is a frictionless torsional suspension; this consists of a metal cube $N$ with a hole for the quartz rod and a clamp screw. The cube is fixed in the stand by two steel plates placed crosswise. This method of attachment excludes simultaneously all three forward motions and two rotations, leaving only one degree of freedom—rotation about the vertical axis which passes through the center of the stand. The lever $C$ is connected to the load $p$ by a wire passing over the brass pulley $O$, which has very low friction. When the lever is moved to one side, a moment of rotation in the opposite direction is set up owing to the existence of an elastic attachment. The load $p$ falls or rises, so moving the thread $b$ connected with it, as the vessel $D$ is emptied or filled with water from the upper reservoir $E$. The supply of water to the vessel is regulated by the micro-tap $K$.

When water flows out of the vessel $D$ through the lower tube with the tap $K_1$, the thread $b$ moves, comes into contact with the thread $a$, and deflects it to a certain (precisely determined) distance from the equilibrium position. At the end of a certain time of contact, as the load $p$ rises (when the vessel is filled from the upper reservoir), the thread $b$ is deflected in the opposite direction. The adhesion force between the polymer-coated quartz threads causes the thread $a$ to move away from the equilibrium position and to follow the motion of the thread $b$. With this apparatus it is possible to increase the force tending to detach one thread from the other, very slowly and smoothly. The deflections of the thread from the equilibrium position are observed with the aid of a

reading microscope $M$ with a micrometer eyepiece and vernier scale for measurement of the thread displacement. To make the instrument stable and to prevent distortion of the experimental results by vibrations, it was placed on a shockproof base. The diameter of the quartz threads was determined after application of the films.

According to Deryagin's theory[6]:

$$N = -\frac{2\pi\sqrt{r_1 r_2}}{\sin\omega} f_0 \qquad (2)$$

where $N$ is the force of adhesion; $r_1$ and $r_2$ are the radii of the threads; $f_0$ is the specific work of separation per unit area; $\omega$ is the angle between the axes; for $\omega = 90°$ we have:

$$N = 2\pi\sqrt{r_1 r_2}f_0 \qquad (3)$$

It is assumed in Formula (2) that $N$ corresponds to point contact, and therefore the values of $f_0$ calculated with this formula for thick films with an appreciable contact area are conventional. Thus, Formula (3) can be used for calculation of the specific adhesion energy $f_0$.

The interaction forces between the polymers were determined in dynes by direct readings of the number of divisions of the micrometer eyepiece calibrated in force units.

The rigidity coefficient of the polymer-coated thread was determined by comparison of two vibration periods: $T_0$ for a free and $T_1$ for an attached pendulum, as described previously[4]. With a known rigidity coefficient of the thread, the divisions of the eyepiece scale can be expressed in dynes after determination of the value of the eyepiece scale divisions in the mixture with the aid of a micrometer lens.

The first part of this work consisted of a study of the effect of film thickness and contact time on the authohesion energy of different rubbers. Natural smoked sheet rubber and synthetic sodium butadiene rubber were used. The results are shown in Figures 3 and 4, where the abscissa axes show the film
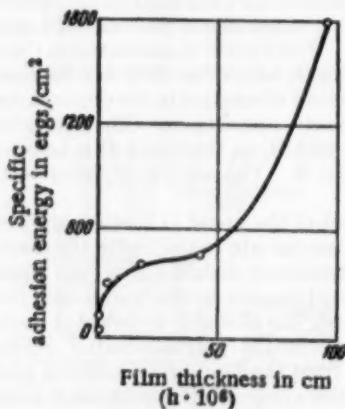


FIG. 3.—Autohesion energy as a function of the thickness of a film of natural smoked sheet rubber. Contact time 60 minutes.
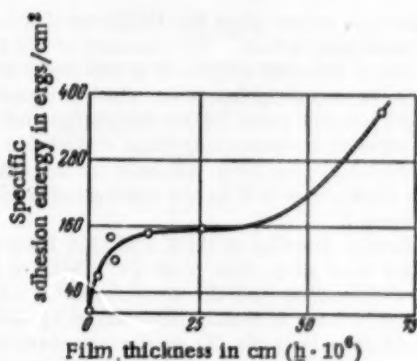
FIG. 4.—Autohesion energy as a function of the thickness of a film of synthetic sodium butadiene rubber. Contact time 60 minutes.

thickness, and the ordinate axes give the specific energy of adhesion (or, more precisely, autohesion).

To show the effect of film thickness on the kinetics of autohesion, Figure 5 shows a plot of the contact time, taken along the abscissa axis, against the specific autohesion energy, taken along the ordinate axis. The different curves represent films of different thicknesses.

### DISCUSSION OF RESULTS

The above results show that the autohesion energy increases with increase of film thickness from 0.01 to $1\mu$. In the thickness range from 0.1 to $0.5\mu$ the autohesion energy does not depend on the thickness (plateau on the curves in Figures 3 and 4). The increase of the autohesion energy in the range from 0 to $0.1\mu$ is probably the result of increasing van der Waals forces between the
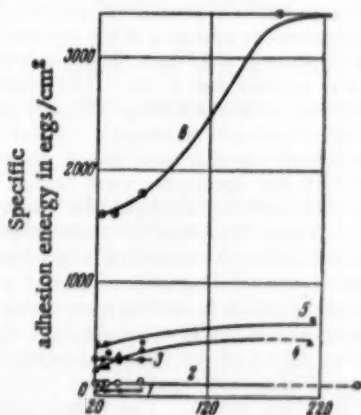


FIG. 5.—Kinetics of autohesion for films of different thicknesses: 1) $0.31 \cdot 10^{-6}$; 2) $1.20 \cdot 10^{-6}$; 3) $2.81 \cdot 10^{-6}$; 4) $16.7 \cdot 10^{-6}$; 5) $41.9 \cdot 10^{-6}$; 6) $94.0 \cdot 10^{-6}$ cm.

rubber films; this increase ceases when the thickness of the polymer layer exceeds the radius of molecular action.   The increase of the adhesion energy at thicknesses $> 0.5\mu$ has a different origin—it is the result of formation of flat areas of contact with the use of thicker films, which are more easily deformed. The formation of such contact areas creates favorable conditions for stress relaxation and coalescence of the contacting films.   With film thicknesses up to $0.5\mu$ increase of contact time has little influence on the autohesion energy of rubbers.   With film thicknesses $> 0.5\mu$ the autohesion energy depends on the contact time (see Figure 5).

The different adhesion kinetics of thick and thin films of rubber may be explained by the fact that when thin films $(< 0.5\mu)$ are applied to quartz threads the contact deformation and the area of contact are both very small. In this case the adhesion force is mainly determined by molecular attraction, which depends, according to Formula (3), on the curvature of the surface, since the contact approximates to point contact; here the effects of contact area and relaxation and chain intertwining processes are unimportant.

On the other hand, with thicker films the contact area becomes fairly extensive, and here intertwining of adjacent chains as the result of intramolecular Brownian movement, and also relaxation and consequent increase of the contact area, may have an influence.   In consequence, the autohesion kinetics of quartz threads coated with thick polymer films becomes similar to the autohesion kinetics studied previously by others for flat surfaces with considerable areas of contact.   By means of the above method it is also possible to distinguish quantitatively between the autohesion of natural and SKB synthetic rubber, both in the region of molecular adhesion, and in the region of autohesion kinetics.   In both regions the autohesion of natural rubber is greater than that of SKB.

## ADHESION OF RUBBERS

To determine whether the relaxation or the diffusion mechanism[9] predominates when the contact area between two polymers is appreciable, experiments on the adhesion between different polymers were carried out.   To avoid the influence of forces of electrostatic origin, which are known to predominate over molecular forces during separation of layers, the adhesion was measured as the force in kg./cm.$^2$ required to move one part of the specimen relative to another. The specimens were fabric strips $5 \times 10$ cm.   The width of the band onto which the polymer solution was applied was 1 cm.   The amount of dry substance applied to 1 cm$^2$ of specimen area was 0.03 g./cm$^2$, one polymer being applied to one strip, and the other polymer to another.   After complete removal of solvent the strips were folded together and placed under a load of 40 g/cm$^2$ for 5 minutes, after which the specimens were tested.   Not less than five specimens were used in each test, the average value being taken.

The following high polymers were used: natural rubber, SKS-30, SKN-26, SKB, butyl rubber, and Nairit.   The method described above was used to determine both the autohesion of these polymers, and their mutual adhesion. The results were compared with data on the compatibilities and polarities of these polymers.   Data on compatibility were obtained from the literature[10–12], mainly based on determinations of mechanical properties, and the following method was also used to determine compatibility.   Solutions of different polymers in the same solvent were mixed.   The mixed solution was thoroughly stirred and observed.   If at the end of a definite time the mixture separated out into layers, it was assumed that the polymers are not compatible.   Finally,

## TABLE I

### CORRELATION BETWEEN AUTOHESION AND COMPATIBILITY

| Polymer | Shearing resistance, kg./cm.² | | | | | |
|---|---|---|---|---|---|---|
| | Natural rubber | Nairit | SKS-30 | SKN-26 | SKB | Butyl rubber |
| Natural rubber | | + − ⊖ 3.20 | + − ⊕ 1.60 | − ⊖ 1.32 | + + ⊕ 0.10 | − ⊕ 1.14 (1.44) |
| Nairit | + − ⊖ 1.60 | 2.0 | − ⊖ 0.58 | − ⊕ 1.00 | − ⊖ 0.30 | − ⊖ 1.08 |
| SKS-30 | + − ⊕ 1.32 | − 0.58 | 1.04 | − ⊖ 0.30 | + − ⊕ 0.60 | − ⊖ 0.80 |
| SKN-26 | − ⊖ 0.10 | − ⊕ 1.00 | − ⊖ 0.30 | 0.48 | − ⊖ 0.28 | − ⊖ 0.62 |
| SKB | + + ⊕ 1.14 | − ⊖ 0.30 | + − ⊕ 0.60 | − ⊖ 0.28 | 0.54 | − ⊕ 0.58 |
| Butyl rubber | − ⊕ 1.44 | − ⊖ 1.08 | − ⊕ 0.80 | − ⊖ 0.62 | − ⊕ 0.58 | 0.36 |

similarity of polarities was taken as the simplest and clearest indication of compatibility.

The results of the tests are shown in Table I, where compatibility is indicated by + and incompatibility by −; the upper sign represents the result of compatibility determination in solution, while the lower, if two are given, represents literature data. In addition, if both polymers are non-polar or both are polar, the sign ⊕ is used, while if one is polar and the other non-polar, the sign ⊖ is given.

### DISCUSSION OF RESULTS

The resistance to shear, which was chosen as the measure of adhesion, may be represented as:

$$T_{12} = S_{12}\tau_{12} \tag{4}$$

where $S_{12}$ is the area of true or molecular contact of the 1st and 2nd polymers and $\tau_{12}$ is their true specific shearing resistance. It is seen that $T_{12}$ depends both on the mechanical properties of the contacting specimens, by virtue of $S_{12}$, and on their specific interaction, which determines the magnitude of $\tau_{12}$. As a result, a complex situation should be produced in the general case.

A more simple and characteristic situation may, however, be obtained for combinations of polymers for which one of the factors in Equation (4) varies little relative to the other. Let us first suppose that $S_{12}$ varies more strongly. Since $S_{12}$ satisfies the conditions

$$S_{11} \geqslant S_{12} \geqslant S_{22}$$

where $S_{11}$ and $S_{22}$ represent the areas of true contact between identical specimens, Specimen 1 being assumed softer than Specimen 2, then $T_{12}$ in Equation (4) will have a value which does not pass appreciably outside the range $T_1, T_2$. If the contact is assumed to be elastic and conforming to the Hertz formula, while the elastic moduli of the two specimens are not too widely divergent in order of magnitude, then $S_{12}$ and consequently also $T_{12}$ will be close to the arithmetic means of the corresponding values of $S_{12}$, $S_{22}$ and $T_{11}$, $T_{22}$. If we suppose that the elastic moduli differ greatly or that the contact is determined by plastic deformation, then $S_{12}$, and therefore also $T_{12}$ will be close to values corresponding to the contact of the softer specimen with a similar one, i.e., $S_{12} \approx S_{11}$, $T_{12} \approx T_{11}$. In any event, irrespective of the mechanical properties of both specimens, $S_{12}$ and $T_{12}$ can never lie outside the ranges of the corresponding values $S_{11} - S_{22}$ and $T_{11} - T_{22}$.

The situation is different if for these combinations of contacting specimens $\tau_{12}$ varies much more than $S_{12}$. Two possible cases must be distinguished here. If the magnitude of $\tau_{12}$ is mainly determined by diffusion and intertwining of the chains of the two polymers, which occur more easily as the polymers become more similar in nature, then evidently $\tau_{12}$ will vary in parallel with the compatibility of the two polymers and in absence of compatibility $\tau_{12}$ may be considerably less not only than $\tau_{22}$, but also in comparison with $\tau_{11} < \tau_{22}$.

There should then be a correlation between compatibility and the ratio $\tau_{12}/\tau_{11}$, as in the case of natural rubber and SKN-26 (Table I). If $\tau_{12}$ is mainly influenced by the interaction of charges of the electric double layer at the boundary between the two specimens, then the values of $\tau_{12}$ may exceed not only $\tau_{11}$ but also $\tau_{22}$, while no parallel should exist between the value of the ratio $\tau_{12}/\tau_{11}$ and the compatibility (SKB + butyl rubber).

It is easily seen in Table I that in the case of adhesion of butyl rubber to other polymers $T_{12}$ is always greater than $T_{11}$. This indicates that diffusion processes have no appreciable influence, and suggests the possible influence both of the contact area, and of the electric double layer. If the case of butyl rubber is omitted from Table I, then combinations of all the other polymers

TABLE II

CORRELATION BETWEEN $T_{12}/T_{11}$ AND COMPATIBILITY

| Polymer pair | $T_{11}$ | $T_{22}$ | $T_{12}$ | $T_{12}/T_{11}$ | Compatibility | | |
|---|---|---|---|---|---|---|---|
| | | | | | in solution | from literature data | from similar polarities |
| Nairit + NR | 2.00 | 3.20 | 1.60 | 0.80 | + | + − | − |
| SKS-30 + NR | 1.04 | 3.20 | 1.32 | 1.27 | + | + − | + |
| SKN-26 + NR | 0.48 | 3.20 | 0.10 | 0.20 | − | − | − |
| SKB + NR | 0.54 | 3.20 | 1.14 | 2.11 | + | + | + |
| SKS-30 + Nairit | 1.04 | 2.00 | 0.58 | 0.55 | − | | − |
| SKN-26 + Nairit | 0.48 | 2.00 | 1.00 | 2.08 | − | | + |
| SKB + Nairit | 0.54 | 2.00 | 0.30 | 0.55 | − | − | − |
| SKN-26 + SKS-30 | 0.48 | 1.04 | 0.30 | 0.62 | − | − | − |
| SKB + SKS-30 | 0.54 | 1.04 | 0.60 | 1.11 | + | + − | + |
| SKN-26 + SKB | 0.48 | 0.54 | 0.28 | 0.58 | − | − | − |
| Butyl rubber + NR | 0.36 | 3.20 | 1.44 | 4.00 | − | | + |
| Butyl rubber + Nairit | 0.36 | 2.00 | 1.08 | 3.00 | − | | − |
| Butyl rubber + SKS-30 | 0.36 | 1.04 | 0.80 | 2.22 | − | | + |
| Butyl rubber + SKN-26 | 0.36 | 0.48 | 0.62 | 1.72 | − | | − |
| Butyl rubber + SKB | 0.36 | 0.54 | 0.58 | 1.61 | − | | + |

show a clear correlation between $T_{12}$ and the compatibilities of the Polymers 1 and 2.

With definite incompatibility, $T_{12} < T_{11}$ in all cases, and conversely, which indicates the role of the diffusion mechanism. This is very convincingly confirmed by the correlation between the values of $T_{12}/T_{11}$ and the compatibilities of the corresponding polymers, as shown in Table II.

The clearest correlation, without any exceptions, is found between the ratio $T_{12}/T_{11}$ and the compatibility index based on the principle of similar polarities. If both polymers are non-polar or both are polar, $T_{12}/T_{11} > 1$, and when one is polar and the other non-polar, $T_{12}/T_{11} < 1$.

The other compatibility indices do not always correlate with the ratio $T_{12}/T_{11}$. It is noticed, however, that these deviations from the general correlation are always accompanied by contradiction of the respective compatibility indices, which shows that these are doubtful in a number of cases. Consequently, the surface compatibility of rubbers, indicated by their adhesional resistance to shear, is most reliably determined by the characteristic of similar polarities. However, butyl rubber does conform to this rule. In the case of Butyl rubber and SKN-26 $T_{12}/T_{22}$ is considerably greater than unity, which may be attributed to specific adhesion due to the electric double layer or van der Waals forces. In the other cases for Butyl rubber $T_{22} > T_{12} > T_{11}$, which may be explained by the influence of mechanical properties on the true contact area.

## SUMMARY

1. The researches so far published on the autohesion of polymers do not make it possible to isolate the influence of the mechanical properties of rubbers, which determine the true area of contact, from the influence of polymer chain diffusion.

2. Studies of the autohesion of thin films of rubber applied by the drain-off method to quartz threads, in relation to the film thickness and contact time, show that for films less than $3.10^{-5}$ cm. thick the adhesion force is small and varies very little with contact time. This proves, on the one hand, that in this instance the contact area is small (which is obvious) and does not increase with time, and on the other hand, that diffusion processes play no part in the autohesion of films of this thickness.

3. The effects which depend on mechanical properties and on the specific interaction (per unit area of true contact) between specimens may be separated if the measured values of adhesion between all possible combinations of pairs of rubbers are compared both with their compatibilities, and with their autohesion.

4. The measurements of the adhesional shearing strength of combinations of different pairs of polymers, carried out for this purpose, showed that the results for Butyl rubber may be interpreted on the assumption that diffusion processes do not play any appreciable role and that the adhesion strength is determined both by the true contact area, which depends on the mechanical properties of the corresponding polymer specimens, and also by the influence of forces associated with the electric double layer.

5. For the other rubbers the results may be interpreted only on the assumption that diffusion processes play a significant part. For similar polarities, $T_{12}/T_{11} > 1$ and for dissimilar polarities, $T_{12}/T_{11} < 1$.

6. General conclusion: autohesion and mutual adhesion of rubbers is deter-

mined both by mechanical properties, which determine the true contact area, and by diffusional properties. The latter are by no means always decisive.

The electric double layer also probably influences the adhesional shearing strength in some instances. It is even more likely to play a role in some cases in measurements of the work of separation of two layers.

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# TACK OF PRESSURE-SENSITIVE TAPE *

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Attempts to put the finger test for film tack on an objective basis have met with considerable success in the printing[1,2] and paint[3] industries. Gainsley and Dow[4] discussed qualitatively the tack and adhesion strength of pressure-sensitive tape. A dash-pot and spring model was presented by Bright[5] for the pressure-sensitive adhesive system.

In the tack test for printing ink, a film of ink is stretched to a cohesive break between two fingers, one finger and a metal surface, or two metal surfaces. Here viscous flow is the dominating factor and elasticity plays an insignificant role. In the case of paint or varnish, tack-free time is used as a measure of drying rate. The prime interest is the time until the film shows no tack, although tack itself is not the chief concern in this case. A film of tackified, partially vulcanized rubber is transversely stretched in the finger test for tack of pressure-sensitive tape. The force resisting separation is limited by the interfacial force instead of by the strength of the film itself as in the case of printing ink. The methods, which are successful for printing ink or paint, might not be suitable for measuring tack of pressure-sensitive tape.

Retardation to the rolling of a steel ball was used as a measure of tack in two testers designed for pressure-sensitive tape, which had been tried in our laboratory. One of them, using a 0.25 inch steel ball rolling over an inclined plane, gave no significant results. A larger ball, 1 inch in diameter, and a curved track was used in the other tester which was constructed according to a blueprint given to this laboratory through the generosity of Douglas Aircraft Corporation. The readings taken from this tester showed large deviations that made the interpretation difficult, as shown in the later part of this paper.

In this work, tack of pressure-sensitive tape is defined as the force resisting peeling when a length of tape is applied on a standard surface under no other pressure than the weight of the tape itself and peeled from the surface with the free end of the tape making an angle of 90° with the surface.

It was noticed under the microscope that during the process of peeling there is a slight depression in the surface of the backing material just before the bend, as shown in Figure 1. In this figure the depression was made prominent by using a very stiff backing material. This effect is also more appreciable when the tape is peeled at an angle of 180° to the testing panel instead of at 90°. A depression in the backing material would press on the adhesive and tend to make the adhesion strength higher. In order to minimize the interference of this effect the peeling is to be done at an angle of 90° in tack testing for pressure-sensitive tape.

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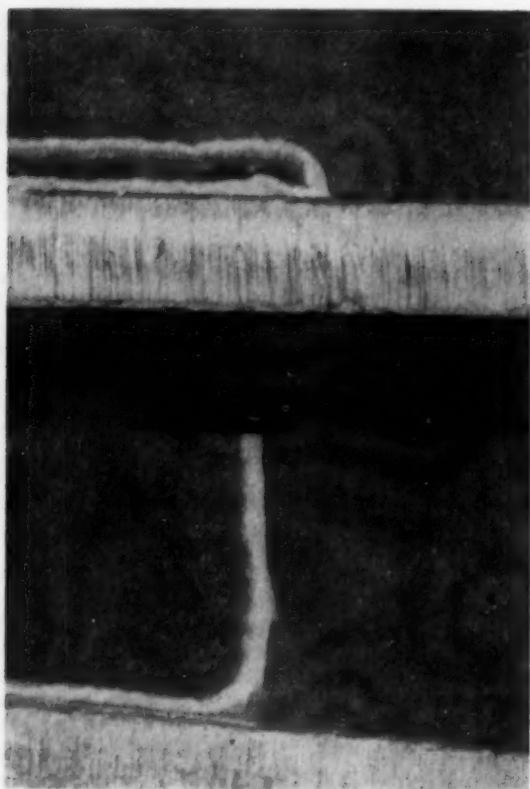
Fig. 1.

## EXPERIMENTAL PROCEDURE

For tack testing, a length of tape sample was held between the two hands with the middle section of the tape hanging down freely.   The tape was lowered gradually and the middle section was allowed to come into contact with a No. 2 finish stainless steel panel.   Then the two ends of the tape were slowly let down so as to assure that the tape was put on the steel panel without any added pressure.   The peeling was done with a Dillon machine[6] at a speed of 12 inches per minute with the free end of the tape at an angle of 90° to the panel.

Adhesion strength of sample tape was measured according to the standard procedure[7] which specifies that the tape should be rolled with a 4.5 pound rubber roller after being applied to the panel and that the peeling angle should be 180°.

All testing in this work was done with 1 inch wide tapes after being conditioned for 24 hours in an atmosphere of 70° F and 50 per cent relative humidity.

## ADHESION STRENGTH AND TACK

Since the testing method for tack stated above is similar to that for adhesion strength, it would be interesting to see what difference there is between

TABLE I

COMPARISON OF TACK WITH ADHESION STRENGTH

| Sample no. | Adhesion strength 180°, oz. | 90°, oz. | Tack as defined, oz. | Tack by finger test |
|---|---|---|---|---|
| 1 | 40 | 26 | 18 | |
| 2 | 35 | 28 | 16 | |
| 3 | 34 | 29 | 19 | High |
| 4 | 31 | 26 | 18 | |
| 5 | 27 | 22 | 7 | Low |
| 6 | 25 | 22 | 11 | Intermediate |
| 7 | 18 | 16 | 0 | |

the adhesion strength and tack of the same tape. Table I shows a comparison of these two properties for a variety of samples.

The data are arranged in order of decreasing adhesion strength with peeling angle of 180° (180° adhesion strength hereafter). The 90° adhesion strength follows approximately the same trend, but the tack does not. This shows that tack is not the same as adhesion strength, 90° or 180°. Or, in other words, the difference between tack and standard adhesion strength, i.e., 180° adhesion strength, is not due to the difference in peeling angles only.

From the group of samples listed in Table I, three were chosen for finger test by experienced individuals in our laboratory. The unanimous results listed in the last column of Table I show a parallelism between tack as defined and results of the finger test.

## PRECISION AND REPRODUCIBILITY

A paper tape was randomly selected as a sample for testing the precision of this method. The test was repeated fifteen times and the results agreed with one another within ±1 oz. This is better than what is generally taken as the precision of the adhesion strength test (about ±2 oz.).

Five of the samples listed in Table I were tested again after a week for reproducibility of data. The two sets of data obtained a week apart are listed in Table II which shows that the reproducibility of the tack test is rather high.

TABLE II

| Sample no. | Adhesion strength Original, oz. | After 1 week, oz. | Tack Original, oz. | After 1 week, oz. |
|---|---|---|---|---|
| 1 | 39 | 38 | 18 | 18 |
| | 41 | 41 | 17 | 17 |
| 2 | 36 | 38 | 16 | 16 |
| | 34 | 34 | 15 | 17 |
| 3 | 35 | 41 | 19 | 19 |
| | 33 | 38 | 19 | 18 |
| 4 | 30 | 36 | 18 | 17 |
| | 31 | 33 | 18 | 19 |
| 5 | 28 | 26 | 7 | 7 |
| | 26 | 27 | 6 | 8 |

## COMPARISON WITH DOUGLAS TACK TESTER

The name used in our laboratory to identify a tester built according to the
blueprint given to this laboratory through the generosity of Douglas Aircraft
Corporation, is the "Douglas tack tester". This tester consists of a flat hori-
zontal aluminum track with one end curved upward. A 1 inch stainless steel
ball is released from the curved part of the track. When it reaches the bottom
of the curve, its motion is retarded by the pressure-sensitive tape laid on the
horizontal part of the track. The length of tape over which the ball rolls be-
fore it comes to a complete stop is taken as an indication of the tack of the tape.

### TABLE III

#### TACK READINGS OF SAMPLE No. 3

| Tack by new method, oz. | Douglas tester, in. |
|---|---|
| 19 | 15.6 |
| 18 | 8.2 |
| 19 | 11.4 |
| 19 | 10.5 |
| 19 | 15.2 |
| 19 | 14.2 |
| Average 19 | Average 12.6 |

The readings taken from this tester show wide fluctuations. Table III
gives an example of these readings. The tack readings of the same tape sample
obtained by the method suggested in this paper are included for comparison.

The data from the Douglas tester in the second column show a standard
deviation of 22 per cent. It would be necessary to take a large number of read-
ings in order to make the average value representative. The new method gives
consistent readings which are listed in the first column of Table III.

In the Douglas tester the higher the retardation, the shorter the distance
measured. If the distance is assumed to be inversely proportional to tack, the
reciprocal of the distance measured would be a direct measure of tack. In order

### TABLE IV

| Sample no. | Tack, oz. | Douglas reading D, in. | Ratio tack | Ratio 1/D |
|---|---|---|---|---|
| 5 | 7 | 31.5 | 1 | 1 |
| 2 | 16 | 14.5 | 2.3 | 2.2 |
| 3 | 19 | 12.6 | 2.7 | 2.5 |

to compare the readings from the Douglas tester and the new method, a sample
tape is arbitrarily taken as the basis. The ratio of tack measured by the new
method to that of sample No. 5 is compared in Table IV to the ratio of the
reciprocal of the distance measured on the Douglas tester to that for sample
No. 5.

It can be seen there is excellent correlation. There is one logical conclusion
from this fact, namely, that if the readings from the Douglas tester are indica-
tions of tack, the new method can also give indication of tack and in a more con-
venient manner.

## THICKNESS OF ADHESIVE FILM

In order to study the effect of various factors on the tack of pressure-sensitive tape, a series of samples were prepared by applying the same adhesive by a solvent deposition method onto papers of different stiffness. Each series consisted of several samples varying in the thickness of the adhesive film. The thickness was not actually measured, but instead, the difference in weights of resulting tape and unprocessed paper of the same area was taken as an indication of the thickness of film, assuming there was no change in weight of paper after the process.

The weight of adhesive on paper is expressed in pounds per ream, one lb./rm. being approximately equivalent to 0.17 mg./sq. cm.

The adhesive used was made of the following ingredients:

| | Parts |
|---|---|
| Natural rubber, No. 1 smoked sheet | 100 |
| Rosin ester | 80 |
| Antioxidant | 1 |
| Filler | 15 |
| Phenol-formaldehyde resin | 8 |

A heat treatment was applied to the sample sheet in a circulating air oven at 250° F for 3 minutes, after the adhesive had been spread on the paper and the solvent driven out under infrared lamps. Strips of 1 inch width were cut from these sheets and used for all tests which were run in the manner explained in the early part of this paper.

Plotting tack versus weight of adhesive, the results of tack testing are reproduced in Figure 2. The technique of least squares was employed to fit a straight line to the points of each series. It was found that the differences among the characteristics of all the three lines are within the limit of experimental error. Hence, one line is used to fit all points. This means that
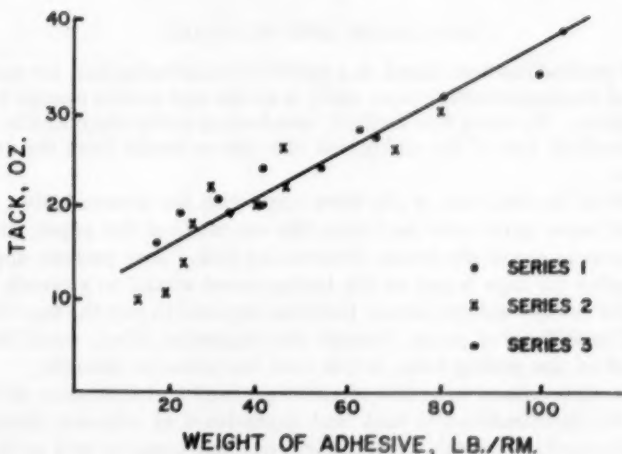


FIG. 2.
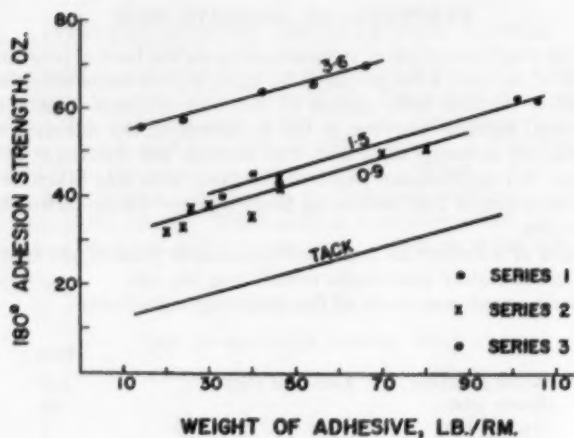
Fig. 3.

within the range of paper and weight of adhesive covered in this experiment, tack is probably independent of paper stiffness.

The case of 180° adhesion strength is different from that of tack, as shown in Figure 3, in which the 180° adhesion strength data are plotted against weight of adhesive, with the stiffness[5] of paper of each series marked on each line. It is evident here that the stiffness of paper used is an important factor influencing the 180° adhesion strength. The fact that these three lines are practically parallel to one another indicates that the slope of the lines is characteristic of the heat treated adhesive. This conclusion finds further support in the fact that the tack line shown at the bottom of Figure 3 is also practically parallel to the 180° adhesion strength lines.

## DISCUSSION AND SUMMARY

A new method has been found, as a result of this investigation, for measuring the tack of pressure-sensitive tape, which is simple and precise enough for practical purposes. By using this method, tack testing yields reproducible quantitative records in lieu of the ambiguous descriptive results from the empirical finger test.

In light of the fact that, of the tapes made with the same adhesive, the one with crepe paper gave lower tack than the one made of flat paper, surface of contact must be one of the factors determining tack. Any pressure applied on the tape after the tape is put on the testing panel would, to a certain extent, increase the contact surface, hence, the force required to peel the tape from the panel. The stiffness of paper, through the depression effect, would have the same effect on the peeling force, in this case, the adhesion strength.

Since tack is defined to be free of added pressure and depression effect, this explains the independence of tack and dependence of adhesion strength on stiffness of paper. Fom this point of view, one may consider tack as the limiting value of adhesion strength.

## ACKNOWLEDGMENTS

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# REVERSIBLE THERMAL EFFECTS DURING THE DEFORMATION OF HIGH POLYMERS *

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The generation of heat during the rapid stretching of natural rubber and the corresponding cooling during relaxation are well known. This heat generation during adiabatic deformation is due to the entropy decrease caused by the orienting of the molecular chains[1].

It has been known for a long time that metals, such as bronze or steel, cool down if stretched adiabatically within Hooke's limit and that they generate heat upon relaxation[2]. In this case the entropy is increased by deformation.

Both phenomena are interrelated thermodynamically[3] with the thermal coefficient of expansion:

$$C_L \left( \frac{dT}{dZ} \right)_{\text{adiabatic}} = -T \left( \frac{dL}{dT} \right)_2$$

$C_L$ = specific heat at constant length $L$
$Z$ = tensile stress
$T$ = temperature in ° Kelvin

The thermal expansion is positive for steel and negative for elongated rubber.

While investigating the heat generation in the flow zone during cold stretching of PVC and of polyamides it was found that the temperature distribution curves indicated a cooling of the material immediately ahead of the flow zone (Figure 1). The interrelation of this effect with the aforementioned reversible phenomena was of interest.
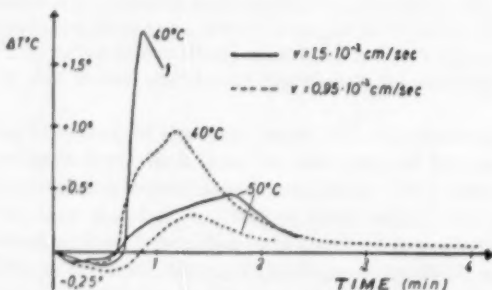


FIG. 1.—Shape of temperature curve for the surface of a PVC sample during cold stretching. The flow zone traveled across a thermocouple touching the film. The registered temperature difference is too small due, according to K. Jäckel, to poor thermal contact and high heat capacity of the thermocouple.
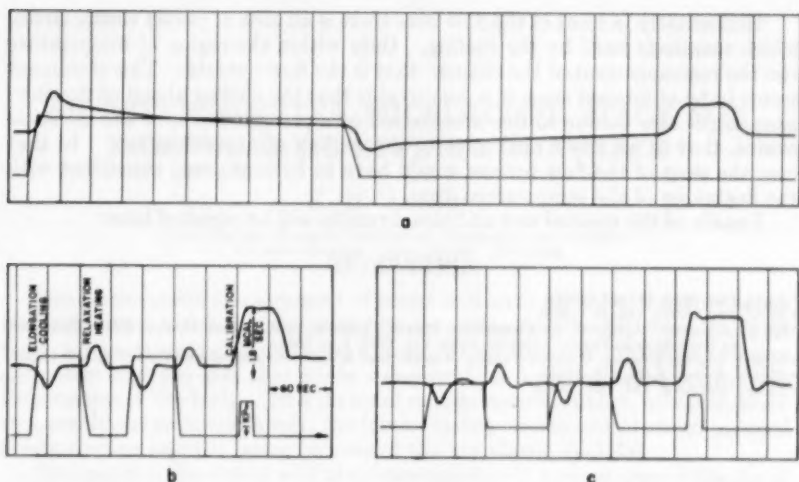
FIG. 2.—Record of stress (lower) and of heat-flow (upper) curves: (a) for natural rubber, (b) for steel wire and (c) for polystyrene oriented parallel to direction of motion. The inscriptions on (b) also applies to the interpretation of (a) and (c). These are drawings made from direct reproductions of autographic curves.

A method, developed in our laboratory for measuring quantitatively the heat evolved during deformation made it possible to solve this problem.   The apparatus is based on the principle of an air thermometer registering with electronic compensation.   Its sensitivity is 0.0001 cal. and its reproducibility in the range of from 0.005 to 0.05 cal. is 10 to 5 per cent.   The apparatus measures primarily heat flowing from the sample.   Therefore it permits certain conclusions as to the relation of time to temperature difference between sample and its immediate environment.   The quantity of heat is calculated as the area integral from the curve recording heat flow as a function of time.   The heat effects to be measured can be positive or negative.   The stress-strain diagram, that is, the mechanical energy of sample deformation, is recorded simultaneously[4].

Figures 2a and 2b indicate the ease with which heat effects occurring in rubber and steel can be recorded with this kind of apparatus.   The results comply, within the error limits, with the aforementioned thermodynamical relation.

Investigations on polystyrene (Figure 2c) show cooling during stretching and generation of heat during relaxation.   The experiments were performed on oriented polystyrene film (Styroflex) of which the direction of orientation was either parallel or perpendicular to the direction of stress.   Both curves indicate basically that polystyrene at room temperature behaves irrespective of orientation in the same manner as steel does in spite of its polymer chain character. In fact it also possesses a positive coefficient of thermal expansion within that temperature range[5].

Unstretched polyamide samples as well as polyvinylchoride give curves similar to 2c when stretched within Hooke's limit.   This proves that the observed cooling[6] ahead of the flow zone during cold stretching is evidently caused by the thermoelastic effect.

Immediately in front of the flow zone there is an area of purely elastic stress, which manifests itself by the cooling.   Only within the region of temperature rise the rearrangement of the chains—that is the flow—starts.   This statement seems to be of interest since it is conceivable that the cooling ahead of the flow-zone might also be due to the cancellation of a preorientation of the molecule chains, that is, an effect analogous to the cooling of natural rubber.   In that case the start of the flow process would have to be considered coincident with the beginning of the temperature drop.

Details of the method and additional results will be reported later.

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# AN EXTENSOMETER MICROSCOPE STAGE FOR
# PHOTOELASTIC STUDIES IN RUBBER *

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The photoelastic measurement of stress in loaded bodies of suitably stress birefringent materials has been highly developed in recent years. In most cases, such measurements rely upon a linear relation between optical retardation and stress and the fact that stress concentration does not cause appreciable deformation of the body. In a material such as natural rubber, however, these two conditions no longer apply, the former failing on account of strain-induced crystallization and the latter because of the low elastic modulus.

This paper is concerned with the determination of stresses around the tip of a tear in a stretched sheet of rubber, and this problem has two important features which arise from the special nature of the material. Firstly, the high extensibility of the rubber limits the region of high stress concentration to very small linear dimensions, of the order of 0.1–0.2 mm. in a typical case. Secondly, the changes in sheet thickness across this region, together with nonlinear stressbirefringence at high extension, demand a more refined technique than simple observation of the isochromatic fringes. Fortunately such a technique is available in the use of a compensator cut from the same sheet of rubber as is the test piece itself, and it is possible by this means to eliminate most of the difficulties encountered with more conventional methods.

These considerations led to the design of the instrument discussed in this paper, which, like the fiber extensometer previously described by the author[1], is designed for attachment to the stage of a polarizing microscope.

## CONSTRUCTION

The extensometer stage is essentially a device for stretching two thin sheets of rubber in mutually perpendicular directions. The planes of the two sheets lie parallel to each other and normal to the incident polarized beam. Each rubber sheet is held between two parallel clamps which slide smoothly along runner bars extending the length of the frame. This is illustrated in Figure 1. The upper pair of clamps is 11 cm. and the lower pair 5 cm. in length, being designed to take differently shaped testpieces as shown in Figure 2. The upper, or "pure shear"[2] testpiece contains a cut or tear, at the tip of which the stress concentration is to be studied, while the lower testpiece is used in simple extension.

The clamps are driven by four independent micrometer screws of pitch 1 mm., their displacements being measured in the usual way. The calibration is such that the separation of a pair of clamps is given directly by adding the readings on their respective micrometers. The method adopted for securing the rubber sheets, which are some 0.2 mm. in thickness, is shown in Figure 3.
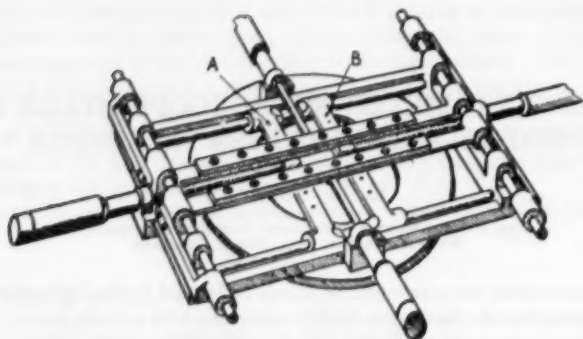
Fig. 1.—The extensometer.

Each clamp consists of a crosshead and a detachable bar, which is fastened to the crosshead by a number of screws to give uniform clamping pressure along its length. While the crosshead surface is flat, the underside of the bar has been milled away so that contact occurs only over a narrow strip along each side of the bar. Its success in preventing slip is due partially to the higher pressure resulting from decreased area of contact, and partially to a more uniform distribution of pressure arising from flexure of the bar.

Each pair of clamps has a minimum separation of 1.0 cm., to avoid fouling the microscope objective at low extensions of the testpiece. The upper pair open to a maximum separation of 4.2 cm. and the lower to one of 9.0 cm.

The rectangular frame of the extensometer stage is bolted to an annular plate of internal diameter 6.4 cm. This plate fits into the stage of a polarizing microscope (by Bausch and Lomb Optical Co., USA) in place of the centering mechanical stage supplied by the makers. The centering mechanism thus operates on the instrument and provides the small but necessary field of view adjustment. The extensometer may also be rotated so that the micrometer barrels lie free of the body of the microscope.
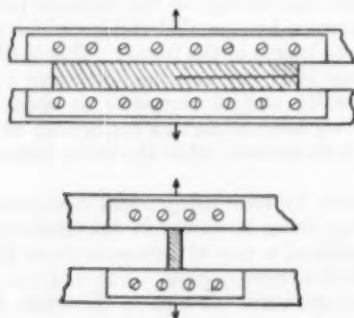


Fig. 2.—The clamps holding differently shaped testpieces.
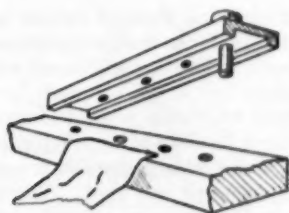
Fig. 3.—Method used to secure rubber sheets in the clamps.

## STRESS IN THE EXTENDED TESTPIECES

In the investigation of stress concentration at the tip of a tear, the test-pieces used are as shown in Figure 2. These are cut from the same sheet of rubber, the tear tip having been formed first and the "pure shear" testpiece, some 8 or 9 cm. by 1.4 cm., marked out around it. The simple extension test piece is approximately 2.0 by 0.4 cm. The state of strain of the "pure shear" testpiece is completely defined by the extension ratio $\lambda$ applied to it, this ratio being given directly by the micrometer readings. In the case of the simple extension testpiece, however, the nominal value of $\lambda$ must be corrected for end effects. Errors in $\lambda$ at high extension could lead to serious miscalculation of stress if this were obtained from independent stress-strain data. For this rea-son, as well as to obviate stress relaxation effects, it was felt advisable to in-corporate some direct means of measuring tension in the lower test-piece. The value of $\lambda$ is still required, of course, for the stress to be known, but it now enters only as a multiplying factor.

The tension measurement is made using a calibrated coiled spring, one end of which is attached by a small clamp to the testpiece and the other to one of the micrometer crossheads $A$. The other end of the testpiece is held as usual by the opposite crosshead clamp $B$. The small subsidiary clamp carries a thin pointer which is aligned with a similar pointer cemented to the frame of the instrument. By keeping the pointer at its null position the extensions of the spring and the test-piece may be read directly from micrometers $A$ and $B$ respectively.

## COMPENSATOR TECHNIQUE FOR MEASUREMENT
## OF STRESS

The state of strain in any small element of the sheet near the extended tip is completely determined by two principal stresses, assuming the stress per-pendicular to the sheet to be zero. The optical retardation of the sheet at that point is

$$r = t \cdot \Delta n \tag{1}$$

where $t$ is the thickness of the deformed rubber and $\Delta n$ the stress birefringence. Since both $t$ and $\Delta n$ are functions of the principal stresses, $P$ and $Q$, this may be written

$$r = f(P, Q) \tag{2}$$

Assuming that the rubber is essentially in simple extension, as is the case near the free edge of the tip, we have $P = 0$ and

$$r = f(Q) \tag{3}$$

If, therefore, a second identical sheet of rubber is subjected to simple extension in a direction perpendicular to that of the element considered, and introduced into the incident beam, extinction will occur when the known value of $Q$ in this "compensator" equals that in the element.

This is the principle upon which the present compensation method is based. In addition to bypassing the difficulties of large deformation and nonlinear stress birefringence, the method also avoids dispersion errors which often arise when compensators of different materials are used. The only complication occurs when the state of strain in the testpiece departs from simple extension, for then the thickness compensation is no longer complete. When this happens it is possible to obtain a solution by determination of the separate stresses, application of a thickness correction and successive approximation, but a discussion of this lies beyond the scope of the present paper.

## EXPERIMENTAL PROCEDURE AND RESULTS

The extensometer, with only the upper testpiece mounted, is fixed in position on the microscope and centered to bring the tear tip into the field of view. The specimen is then extended to the desired amount and the adjustable condenser system of the microscope set to give a nearly parallel beam of light. The apparatus is now ready for photographic record to be made of the isoclinic fringes which appear at different positions as the crossed polarizer and analyser are rotated together. Using a 35 mm. strip film camera with side-viewing tube, the fringes are photographed at each fresh rotation through a known angle, usually 2° or 5° according to the sensitivity of the fringe pattern to such rotation. A low power objective giving a comparatively large field of view is best for this part of the investigation.

When the isoclinics have been photographed, the extensometer is removed from the microscope in order to mount the simple extension testpiece. As this compensator testpiece is extended a black fringe appears behind the tip in the tear testpiece. Using an eyepiece scale its position and width are recorded as functions of the compensator extension and tension, measured as already de-
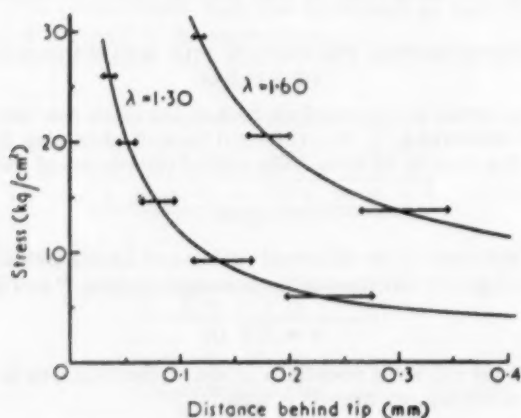


Fig. 4.—Stress concentration curves at different extensions of the testpiece.
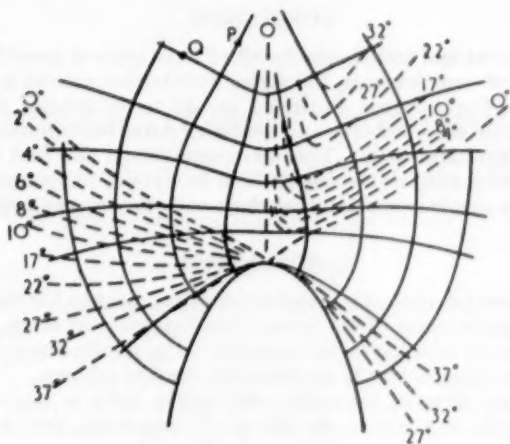
FIG. 5.—Isoclinics (shown dotted) and lines of principal stress at λ = 1.10.
Magnification × 35.

scribed. From this data a graph of principal stress difference against distance
behind the tear tip may be readily obtained. In plotting this curve it is as-
sumed that each edge of the black fringe represents a deviation from the nominal
stress of the same magnitude though, of course, of opposite sign. This enables
the curve to be well defined even in regions where the black fringe is diffuse.
Figure 4 illustrates this for two different extensions of a tear testpiece of pre-
vulcanized latex, to which material the results given below also refer.

The isoclinic patterns obtained photographically are superimposed by
sketching in the projected images on a large sheet of graph paper, an epidia-
scope (by Aldis Bros., Ltd.) being used for this purpose. From the completed
map the lines of principal stress are deduced, as shown in Figure 5. The be-
havior of these lines may be used in conjunction with the curve of principal
stress difference to calculate the separate stresses using the Lamé-Maxwell
equation[3]. Such a calculation suggests (a) that the stress component perpen-
dicular to the direction of stretch rises slowly from zero to its value in the body
of the test-piece and (b) that its magnitude is such that a considerable region
near the tip is essentially in simple extension. This behavior is sketched in
Figure 6 and is in contrast to that found[4] under similar circumstances in a rigid
material.
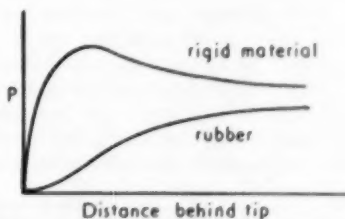


FIG. 6.—Behavior of the minor principal stress P.

## CONCLUSION

The instrument and techniques described have made it possible to solve, to a good degree of completeness, the stress distribution around a tear tip in a rubber sheet. The methods employed should be of general application to materials in which deformability and nonlinear stress birefringence exclude the usual stress-optical approach. The instrument should also find application in more general fields such as the comparison, by optical compensation, of stress birefringence in simple extension, pure shear and other more complicated states of strain.

## SUMMARY

The instrument described is designed for attachment to the stage of a polarizing microscope in place of the conventional mechanical stage. Its purpose is to permit the use of a special compensator technique to determine stress distribution at the tip of a tear in an extended sheet of rubber.

Examples are given of the stress distribution, both in magnitude and direction, at the tip of a tear in prevulcanized latex sheet, and the relative behaviors of the two principal stresses are briefly discussed.

## ACKNOWLEDGMENTS

The author wishes to thank Mr. A. Giles and Mr. E. Giles for the actual construction of the instrument.

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# THE TENSILE STRENGTH OF ELASTOMERS *

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## INTRODUCTION

The critical dependence of the tensile strength of elastomers on their crystallizability has long been recognized, and recent observations on the effect of primary molecular weight[1] and on the effect of the degree of crosslinking[2] on the tensile strength of polyisobutylene and natural rubber, respectively, have been satisfactorily interpreted on a basis of the effect of these variables on crystallizability. These results, while of fundamental significance, still beg the issue somewhat since the question of why crystallization has such a profound effect on strength remains essentially unanswered. Crystallizable elastomers, even at their ultimate elongation, contain a large fraction of amorphous material which might be expected to act as flaws or weakest links, resulting in a weak material. Furthermore, since the crystal phase is present as distinct crystallites and not as a continuous crystal matrix, the assumption that the crystal phase alone supports the stress is untenable. It must be concluded therefore that the strength of the amorphous network is in some way enhanced by the presence of crystallites. In order to determine the nature of this reinforcement, we must first discover the factors which significantly effect the strength of amorphous elastomers. Ideally, a study of the effect of the degree of crosslinking, primary molecular weight, molecular weight distribution, polymer constitution, environment, the presence of additives, and temperature on strength would be required. The present work, being concerned mainly with the effect of crosslinking and temperature on strength, represents only a first step along this somewhat melancholy path. In a sense, however, the last step was taken also by the inclusion of similar studies on crystallizable elastomers and the attempted interpretation of the reinforcing effect of crystallites on a basis of a proposed theory of the strength of amorphous elastomers.

## EXPERIMENTAL

The polymers studied were natural rubber (smoked sheet), a 122° F GR-S containing 22 per cent bound styrene, a 50° C polybutadiene, and a 5° C polybutadiene. Extraneous material was removed from the crude polymer by alcohol precipitation of the polymers from their filtered benzene solutions. Vulcanization was effected through the use of a quantitative crosslinking reagent, decamethylene dismethylazodicarboxylate, using essentially the solution casting technique described by Flory[3]. The vulcanizates prepared in this fashion are of composition 100 grams polymer, 1 gram phenyl-2-naphthylamine (antioxidant), $P$ grams decamethylene dismethylazodicarboxylate, hence are
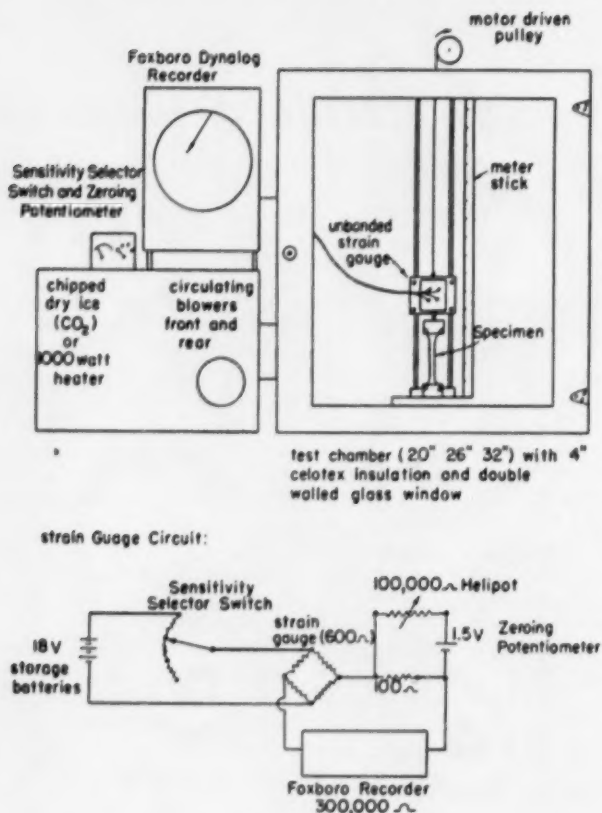
Fig. 1.—Tensile test apparatus.

fully described by the single variable $P$, hereinafter referred to as the per cent disazo.

Tensile strengths were determined at a fixed rate of elongation (0.3 in./sec.) using the apparatus depicted schematically in Figure 1. Controlled temperatures from $+80°$ C to $-50°$ C were obtained by circulating the working chamber air over a 1000 watt electric heater or chipped dry ice. Below room temperature, control to $\pm1°$ C was maintained by manual variation of blower speeds while, above room temperature, control to $\pm0.5°$ C was maintained by a Fenwall thermoswitch, activating the heater, located in the working chamber. The stress sensing element was an unbounded strain gage[4] in most cases, although in the early work on GR-S a cantilever beam attached to the core of a differential transformer was used. The wiring diagram for the strain gauge assembly is illustrated in Figure 1. A variation in sensitivity of from 1 gram/recorder division to 32 grams/recorder division with an error of less than 2 per cent of full scale (50 divisions) could be obtained by changing the input voltage to the strain gage or changing the strain gage. Two strain gages, 4 oz. and 48

oz. capacity, respectively, permitted measurement of tensile strengths of from 100 to 3000 pounds per square inch on the test specimens, which had initial cross-sections of from 0.0005 to 0.002 square inch.

Both ring and dumbbell shaped specimens were used. The dumbbell specimens were 5.88 cm. in length—very nearly identical in size and shape to those used by Flory[2]. The ring specimens were of two sizes of approximate mean diameter 1 inch and 1 centimeter, respectively. Only the room temperature measurements on GR-S were made using dumbbell specimens. The change from dumbbell to large ring to small ring specimens was dictated mainly by space requirements, for the total elongation of dumbbell specimens of the lightly vulcanized polymers was over 100 centimeters from clamp to clamp. The thickness of the died specimens, which ranged from 0.005 to 0.020 inch, was measured on a dial micrometer, which was graduated in 0.0005 inch divisions and could be reasonably interpolated to 0.0002 inch. The specimen width was assumed a constant equal to the die dimension—0.100 inch for the dumbbell, 0.105 inch for both ring specimens.

The tensile strength is given in pounds per square inch initial cross-section, and each graphic point is an average of at least three and in most cases five or more determinations. The standard deviation from the mean of 424 tests was found to be 15.8 per cent, which is considered satisfactory in view of the fact that the maximum random error from all physical measurements involved in a single test is estimated to be about 8 per cent. The ultimate elongation was obtained only approximately by the observation of the position of the upper clamp at rupture.

<center>RESULTS</center>

The effect of the degree of crosslinking on the tensile strength of amorphous elastomers is illustrated in Figure 2 where the tensile strength of GR-S and 5° C polybutadiene is given as a function of the per cent disazo at 30° C. (In most cases, the experimental results are given in graphic form. Duplicate tables of the original data will be supplied to those interested upon request.) The polybutadiene is known to crystallize at reduced temperatures, however x-ray and
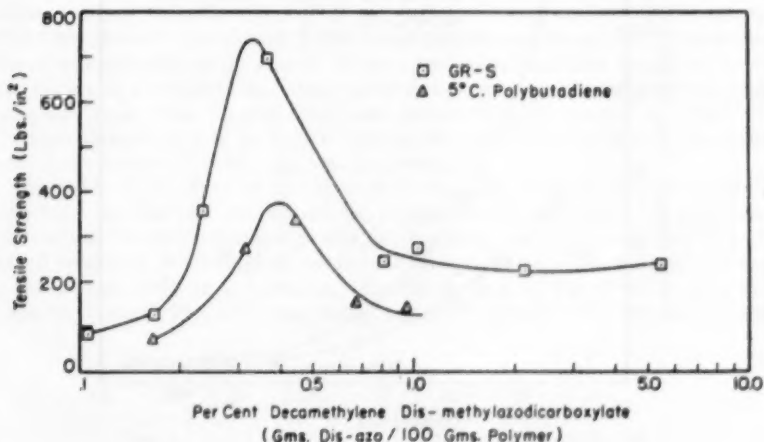


Fig. 2.—Tensile strength at 30° C vs. degree of crosslinking.
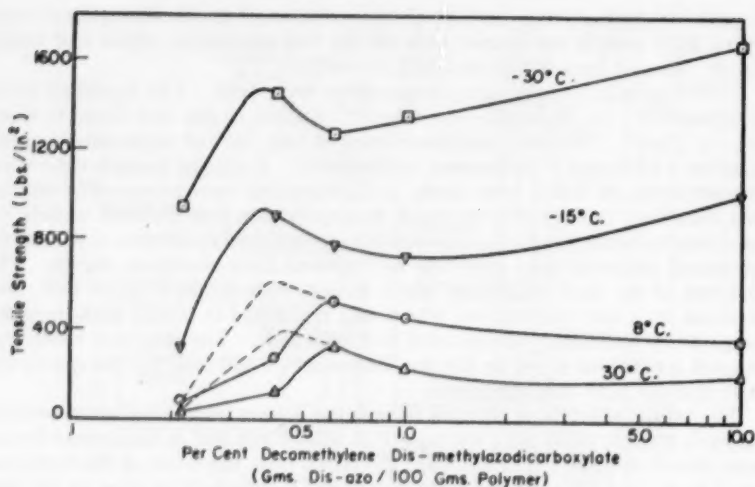
FIG. 3.—Tensile strength of 5° C polybutadiene vs. degree of crosslinking.

birefringence investigations carried out in this laboratory (to be published in
the near future) indicate that it is less than 2 per cent crystalline at 600%
elongation at 25° C.   Its low strength can be taken as indirect substantiation
of its amorphous nature at this temperature.   Fairly conclusive evidence that
it is amorphous at this temperature is given in Figure 4, where the effect of
temperature on the strength of 0.90 per cent disazo vulcanizates of both 5 and
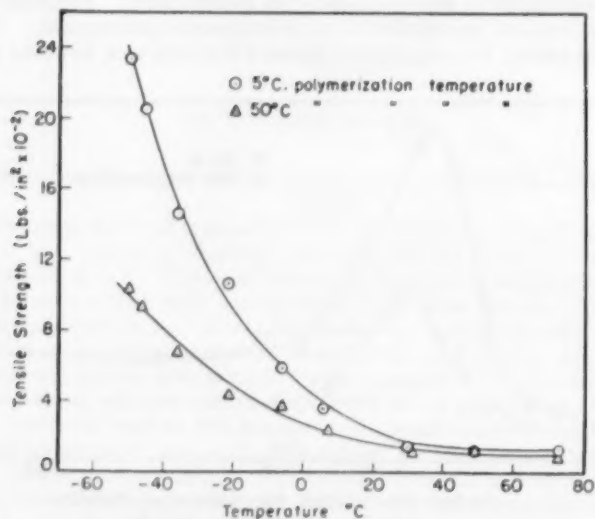


FIG. 4.—Tensile strength of polybutadiene crosslinked with 0.90 per cent
decamethylene dismethylazodicarboxylate
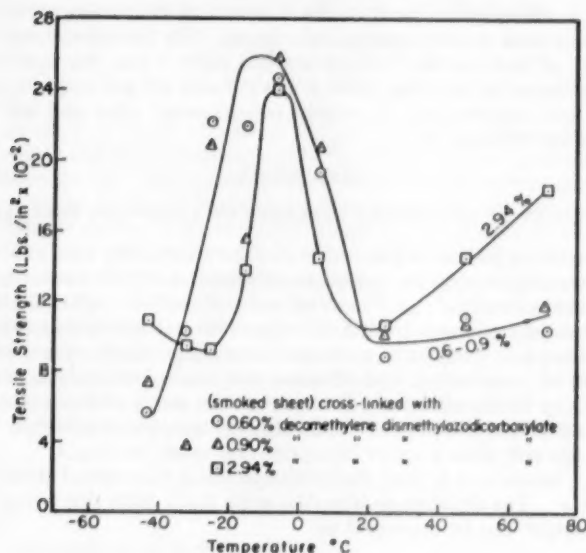
Fig. 5.—Tensile strength of natural rubber.

50° C polybutadiene is shown. The 50° C polymer has not been known to crystallize under any conditions, whereas our measurements indicate that the 5° C polymer is about 19 per cent crystalline at −20° C at 600% elongation. Since the polymers are quite similar, differing principally in the relative ratios of 1,4, 1,2, *cis* and *trans* additions, the large difference in strength at reduced temperatures can be attributed to the crystallizability of the 5° C polymer. It can be seen that they are of essentially the same strength above 30° C.

In Figures 3 and 5, the effect of temperature on the tensile strength of a series of disazo vulcanizates of 5° C polybutadiene and natural rubber respectively are shown. In Figure 3, the experimental results on the 0.4 per cent disazo vulcanizates at 30 and 8° C are questioned, and the expected trends (see Figure 2) are dashed in. This particular series of measurements was made using the large diameter ring specimens, and in the two cases in question, the ultimate elongation was so large it became necessary to double the ring specimen—an admittedly very questionable procedure.

In Table I, the type of specimen used for each series of measurements is recorded. As has been mentioned, the change from dumbbell to ring specimens was dictated mainly by space problems; however, another factor was the observed tendency for dumbbell specimens of the stronger vulcanizates to tear at the clamp, yielding low results. Extensive tests of the effect of specimen shape on strength were not undertaken, but comparison of the overlapping data

TABLE I

| Data of | Obtained using |
|---|---|
| Figure 2 | Dumbbell specimens |
| Figure 3 | 1 inch diam. ring specimens |
| Figures 4 and 5 | 1 cm. diam. ring specimens |

of Figures 2 and 3 indicates that the 1 inch ring specimens yield strengths slightly higher than do the dumbbell specimens.   On the other hand, the average strength of five dumbbell specimens and eight 1 cm. ring specimens of a 1.0 per cent disazo vulcanizate of GR-S was 277 and 235 psi, respectively.   The differences are, however, almost within experimental error and are therefore not of great significance.

## DISCUSSION

### A THEORY OF THE TENSILE STRENGTH OF AMORPHOUS POLYMERS

The interesting feature of the curves of Figure 2 relating the tensile strength of amorphous polymers to the degree of crosslinking is their similarity in shape with the curves obtained by Flory[2] on natural rubber.   Quantitatively, the curves for the amorphous polymers differ from the natural rubber curve in that the amorphous polymers have a sharper maximum which occurs at a much lower degree of crosslinking, and of course the amorphous polymers are much weaker.   Flory has qualitatively interpreted the shape of the natural rubber curve by considering the effect crosslinking has on crystallizability.   Patently for amorphous polymers another interpretation must be sought.

The view taken here is that chain orientation is the critical strength determining factor.   The simplest assumption to be made from this point of view is that the strength can be expressed as:

$TS$ = $K$(total number chains/volume) (fraction orientable chains) (orientation factor)

    = $KN\omega_a\omega_0$

From Flory's theory[1]:

$N$ = total number chains/volume = $(1/M) + (1/M_c)$

$\omega_a$ = the fraction active or orientable chains = $1 - (2M_c)/(M + M_c)$

$$N\omega_a = \frac{1}{M_c} - \frac{1}{M} = \frac{1}{M}\left(\frac{M}{M_c} - 1\right)$$

where $M$ = number-average molecular weight of the uncrosslinked polymer, $M_c$ = molecular weight of the vulcanizate per crosslinked unit and, from the stoichiometry of disazo crosslinking:

$$(M/M_c) = MP/20,100$$

where $P$ = (weight disazo/weight polymer) $\times$ 100.

It is to be noted that Flory emphasizes the $\omega_a$ term in his work on polyisobutylene[1], although he observes that the data are fit equally well by a linear relation between tensile strength and $(1/M)$, that is, the $N\omega_a$ term above, since $M_c$ is constant in his work.

It now remains to determine the nature of the orientation factor.   The strong assumption made here is that, at rupture, the major portion of the stress is determined by the number of chains which have undergone a relative extension very nearly equal to the observed relative extension of the specimen.   Some justification for this assumption can be found by considering the stress-strain relation for a single statistical chain in the region where the Gaussian approximation no longer holds.   That is, when recognition is taken of the finite

ultimate elongation of a statistical chain, the stress is given by[5]:

$$f = \frac{kT}{l} L^{-1}\left(\frac{r}{nl}\right)$$

where $f$ = stress, $l$ = length of a chain link, $n$ = number of links in the chain, $r$ = chain end to end displacement, and $L^{-1}(r/nl)$ = inverse Langevin function of the argument $r/nl$.  The stress on such a chain rises explosively as $(r/nl)$ approaches one, or as the ultimate elongation is approached; hence the stress on a collection of chains (near rupture) would be due mainly to those chains which are extended very nearly to their ultimate elongation.

If it is assumed that the chain displacement vectors in a polymer vulcanizate undergo an affine deformation during extension, a mathematical expression for the orientation factor can be obtained.    In this case, the assumption made in the above paragraph is equivalent to assuming that only those chains whose displacement vectors are oriented at a small angle $\delta$ or less to the direction of extension support the stress at rupture.    Now, in an affine extension, the fraction of chains oriented at an angle $\theta$ to the direction of stretch is given by:

$$\frac{dN}{N} = \frac{\lambda^3}{2}\frac{\sin\theta\,d\theta}{(\lambda^3 - (\lambda^3 - 1)\cos^2\theta)^{\frac{3}{2}}}$$

where $\lambda$ = extension ratio, and therefore:

$$\omega_0 = 2\int_{\theta=0}^{\theta=\delta}\frac{dN}{N} = 1 - \frac{\cos\delta}{(\lambda^3\sin^2\delta + \cos^2\delta)^{\frac{1}{2}}}$$

If the angle $\delta$ is sufficiently small:

$$\omega_0 \doteq 1 - \frac{1}{(1 + \delta^2\lambda^3)^{\frac{1}{2}}}$$

The complete expression for the tensile strength of amorphous polymers then becomes:

$$TS = \frac{K}{M}\left\{\frac{M}{M_c} - 1\right\}\left\{1 - \frac{1}{(1 + \delta^2\lambda^2{}_B)^{\frac{1}{2}}}\right\}$$

where the subscript $B$ is placed on $\lambda$ to indicate that it is the extension ratio at break.    A comparison of this theoretical expression with experiment is given in Table II and Figure 6.    The experimental results are taken from the smooth curve through the GR-S data of Figure 2.    Also, the extension ratio at break is taken from a smooth curve through experimental data.    The molecular weight of the GR-S was not measured, however, its number average is certainly between 100,000 and 200,000; the number used was 120,600 which is not unreasonable and simplifies calculations.    This leaves the parameters $K$ and $\delta$ to be chosen to obtain the best agreement.    From Figure 6, it can be seen that quite good agreement between theory and experiment up to 1 per cent disazo is obtained when $\delta^2$ is given the value 1/20,000—which corresponds to an angle of 0.4°—indicating that the only nearly perfectly oriented chains contribute significantly to the observed strength.

An admitted shortcoming of the above comparison is that the experimentally observed ultimate elongations were used in the theoretical expression.

TABLE II

COMPARISON OF THEORETICAL AND EXPERIMENTAL TENSILE
STRENGTH OF GR-8

| % diazo | Ultimate extension ratio $(\lambda_B)^a$ | Tens. str.,[b] psi | $(6P-1)\omega_c^c$ | Tens. str. (expt.) $\div 4365$ |
|---------|---------|---------|---------|---------|
| 0.2 | 30 | 193 | 0.0696 | 0.442 |
| 0.25 | 25.8 | 468 | 0.1330 | 0.1072 |
| 0.3 | 22.3 | 706 | 0.1584 | 0.1617 |
| 0.35 | 19.8 | 730 | 0.1672 | 0.1672 |
| 0.4 | 17.67 | 634 | 0.1610 | 0.1452 |
| 0.45 | 15.82 | 562 | 0.1469 | 0.1288 |
| 0.5 | 14.36 | 501 | 0.1336 | 0.1147 |
| 0.6 | 11.41 | 400 | 0.0916 | 0.0916 |
| 0.8 | 8.52 | 272 | 0.0574 | 0.0623 |
| 1.0 | 6.52 | 250 | 0.0343 | 0.0573 |
| 5.0 | 2.50 | 238 | 0.0115 | 0.0545 |

[a] Taken from a smooth curve through experimental data.
[b] Taken from a smooth curve for GR-8 in Figure 2.
[c] $P$ = per cent diazo; $\omega_c = 1 - (1 + \lambda_B^2/20,000)^{-\frac{1}{2}}$.

Ideally, we should obtain $\lambda_B$ as a function of primary molecular weight and degree of crosslinking. An only moderately successful approach to this problem is as follows: Since we have assumed that only the well oriented chains are of importance, and that they are nearly at their ultimate extension when the specimen ruptures, the theoretical extension ratio at break equals the ultimate extension ratio of a chain since well oriented chains undergo the same relative extension as the specimen. The chain's length in the undeformed specimen is given by $\overline{r^2}_0 = nl^2$ and ultimate extension of a single chain (neglecting valence angle correction and excluded volume effects throughout) is $nl$, $n$ being the number of links per chain and $l$ the length of a link[6]. Thus $\lambda_B = nl/(\overline{r^2}_0)^{\frac{1}{2}} = (n)^{\frac{1}{2}}$. Furthermore, $(n)^{\frac{1}{2}} = M'_c/M_l$, where $M_l$ = molecular weight per link, and $M'_c$, the molecular weight per chain, is given by[1] $MM_c/(M + M_c)$. From this
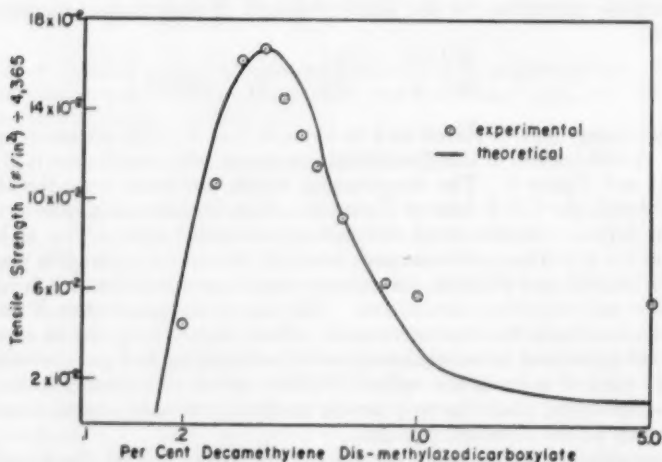


FIG. 6.—Tensile strength of GR-8 vs. degree of crosslinking.

we obtain:

$$\lambda_B = \left(\frac{M}{M_l}\right)^{\frac{1}{2}}\left(1 + \frac{M}{M_c}\right)^{-\frac{1}{2}}$$

as the theoretical expression for the ultimate extension ratio. Setting $M_l = 59.1$ (22% styrene, 78% butadiene) and $M = 120,000$, the calculated $\lambda_B$ is 30.4 at $P = 0.2$ compared to the observed value of 30, however at higher degrees of crosslinking the calculated $\lambda_B$ becomes progressively larger than the observed value. At $P = 1.0$, $\lambda_B$ (calculated) $= 17$, $\lambda_B$ (observed) $= 6.5$. The failure is not surprising in view of the crudeness of the theory. The molecular weight per link is an uncertain quantity, and the inclusion of excluded volume effects changes the functional dependence of $r_0$ on $n$. Furthermore, Treloar[6] states that the ultimate extension ratio of a network of non-Gaussian chains exceeds the extension ratio of the chain by about 25 per cent.

This concept of the ultimate extension leads to a simple and interesting conclusion concerning the effect of swelling on strength, for, if it is assumed that the mechanism of rupture (see below) is unchanged by the swelling agent, its only effect is on $r_0$ and hence on $\lambda_B$. Thus:

$$(\lambda_B)_S = (\lambda_B)_D(SR)^{-\frac{1}{3}}$$

where $(\lambda_B)_S = $ ultimate extension ratio of the swollen vulcanizate, $(\lambda_B)_D = $ ultimate extension ratio of the dry vulcanizate, $SR = $ volume swollen polymer/volume dry polymer, and:

$$(TS)_S/(TS)_D = (\omega_0)_S/(\omega_0)_D$$

where the swollen tensile strength is to be calculated on the dry cross-section.

### THE MECHANISM OF RUPTURE

The apparent success of the foregoing theoretical treatment of the tensile strength of amorphous polymers poses an immediate question. Why does the specimen break when such a small fraction of the chains across a given cross-section break? An explanation of this seeming anomaly is found in the following postulated mechanism of rupture: When a given chain ruptures, presumably the broken ends are active chemical species—ionic or free radical. Because of the cage effect, the chain ends do not separate a great distance before they contact neighboring chains with which they can react. If the reaction causes
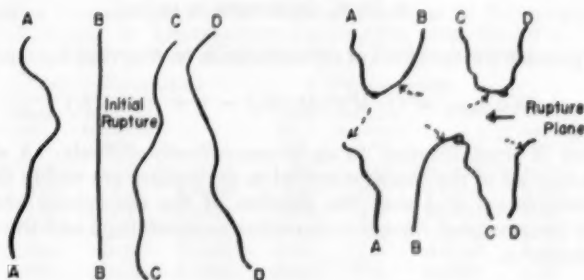


FIG. 7.—Schematic representation of rupture mechanism.

rupture of additional chains, a rapid failure of the specimen in tear might result. For example, assuming the broken ends to be free radicals, and the reaction with neighboring chains to be rapid chain transfer, the mechanism of rupture can be illustrated roughly as is shown in Figure 7. A mathematical formulation of such a process would be similar to that of an autocatalytic reaction, for the product of chain rupture catalyzes chain rupture. The constant $K$ in the expression for tensile strength somewhat inadequately covers the results of such an analysis, for it clearly is some complicated function of temperature, the energies of activation for the two processes involved in rupture, the rate of elongation, etc.

### THE EFFECT OF CRYSTALLIZATION ON STRENGTH

In view of the foregoing theory of the strength of amorphous elastomers the effect of crystallization on strength can be considered to be its effect on the four factors $K$, $N$, $\omega_a$, and $\omega_0$. The product $N\omega_a$, the total number of active chains per unit volume, can be approximately treated as follows: Each crystallite increases the number of active chains by $n$, where $n$ is the number of chains involved in the crystallite; i.e., if the center segments of an amorphous chain become involved in a crystal, two shorter chains replace the single long chain. Thus, the increase in $N\omega_a$ is given by:

$$\Delta(N\omega_a) = \text{(number of crystallites/unit volume)}\,\text{(number of chains in crystallite)}$$
$$= (f_c/v_c)\,(mA_c/a_c) = (f_c/l_c)\,(m/a_c)$$

where $f_c$ = volume fraction crystalline, $v_c$ = volume of a crystallite, $A_c$ = area of a crystallite perpendicular to the fiber axis, $a_c$ = area of crystal unit cell perpendicular to the fiber axis, $m$ = number of chains in the unit cell, and $l_c$ = length of crystallite along fiber axis. Thus:

$$(N\omega_a)_{cryst} = (N\omega_a)_{amorph} + (f_c/l_c)(m/a_c)$$
$$= [(M/M_c) - 1] + (f_c/l_c)(m/a_c)$$

Using the results of Bunn[6] and Hengstenberg and Mark[5] for natural rubber, namely, $m = 4$, $a_c = 110.8 \times 10^{-16}$ cm.², and $l_c = 600 \times 10^{-8}$ cm., the magnitude of the second term, which can be assumed approximately valid for all crystallizable rubberlike elastomers, is:

$$\Delta(N\omega_a) = 6.02 \times 10^{19} f_c$$
$$\doteq 10^{-4} f_c \text{ (expressed in moles)}$$

The final expression for the effect of crystallization on $N\omega_a$ then becomes:

$$(N\omega_a)_{cryst} = (1/M)[(M/M_c) - 1 + 10^{-4} Mf_c]$$

The effect of crystallization on $\omega_0$ is conceptually difficult. A simple assumption is that all of the chains involved in crystallites are within the angle $\delta$ of perfect orientation and that the fraction of the amorphous chains thus oriented can be calculated from the expression $\omega_0$ involving $\delta$ and the extension ratio at rupture, i.e.:

$$(\omega_0)_{cryst} = f_c + (1 - f_c)(\omega_0)_{amorph}$$

where:

$$(\omega_0)_{amorph} = 1 - (1 + \delta^2\lambda^3{}_B)^{-\frac{1}{2}}$$

and $\lambda_B$ = extension ratio at break for the partially crystalline material.

A suitable treatment of the effect of crystallization on $K$ has not been found. However, if it is assumed that the mechanism of rupture is not changed by partial crystallization, $K$ can be assumed unchanged. In this case, the complete expressions for the tensile strength of partially crystalline elastomers becomes:

$$TS = (K/M)[(M/M_c) - 1 + 10^{-4} Mf_c](f_c + (1 - f_c)\omega_0)$$
$$\omega_0 = 1 - (1 + \delta^2\lambda^3{}_B)^{-\frac{1}{2}}$$

which reduces to the expression for the tensile strength of amorphous materials when $f_c = 0$.

A simple, though not entirely satisfactory, test of this expression can be obtained by comparing the strength of 50° and 5° C polybutadiene (Figure 4). If it is assumed that the strength of the 50° C polymer is the same as would be that of the 5° C polymer were it not partially crystalline (which is true above 30° C where neither polymer crystallizes), the fraction crystallinity at rupture as a function of temperature for the 5° C polymer can be calculated. Assuming they are both of primary molecular weight 120,600, $(M/M_c) = 5.4$ $(P = 0.9)$, and we have:

$$R = \frac{(4.4 + 12.06f_c)(f_c + \{1 - f_c\}\omega_0/c)}{4.4\,\omega_0/a}$$

where $R = TS$ (5° C polybutadiene)$/TS$ (50° C polybutadiene) and $\omega_0/c$ and $\omega_0/a$ are calculated from the extension ratio at break for the crystalline (5° C) and amorphous (50° C) polymers, respectively, using $\delta^2 = 1/20,000$ as for GR-S. The results of these calculations are summarized in Table III. It can be seen that the calculated per cent crystallinity is too low. The fact that the calculated per cent crystallinity goes through a maximum, however, is quite reasonable since the rate of crystallization is similarly dependent on temperature. In the last column of Table III, the sensitivity of the calculations to the values chosen for $l_c$ and $\delta$ are shown. In this case, $l_c = 900$ Å instead of 600 Å, and $\delta = 10^{-2}$ instead of $0.705 \times 10^{-2}$. Considering the number of approximations involved, the fact that the calculated per cent crystallinity appears to be

TABLE III

FRACTION CRYSTALLINITY OF 5° C POLYBUTADIENE AT RUPTURE AS A
FUNCTION OF TEMPERATURE CALCULATED FROM RELATIVE
STRENGTHS OF 5° C AND 50° C POLYBUTADIENE

| Temp., °C | 50° C polybutadiene | | | 5° C polybutadiene | | | Calc. per cent crystallinity for 5° C PBD |
|---|---|---|---|---|---|---|---|
| | Tens. str., psi | Ultimate extension ratio | $\omega_0$ | Tens. str., psi | Ultimate extension ratio | $\omega_0$ | |
| 6 | 233 | 10.2 | 0.0253 | 363 | 8.6 | 0.0157 | 2.18 | 4.3[a] |
| -6 | 376 | 12.4 | 0.0440 | 590 | 8.2 | 0.0186 | 4.50 | 8.0 |
| -21 | 438 | 11.1 | 0.0329 | 1070 | 8.9 | 0.0234 | 4.87 | 8.9 |
| -36 | 677 | 11.8 | 0.0385 | 1460 | 7.6 | 0.0109 | 6.09 | 11.2 |
| -45 | 934 | 10.8 | 0.0301 | 2050 | 7.6 | 0.0109 | 4.80 | 8.9 |
| -50 | 1040 | 10.5 | 0.0282 | 2340 | 7.3 | 0.0099 | 4.68 | 8.6 |

[a] Per cent crystallinity calculated using $l_c = 900$ Å, $\delta = 10^{-2}$. See text.

TABLE IV

COMPARISON OF THE EXPERIMENTAL AND THEORETICAL TENSILE
STRENGTHS OF NATURAL RUBBER [a]

| $10^4/M_c$ | Tens. str., kg./mm.² | Extension ratio at break | $f_c$ | Theor. tens. str.[b] |
|---|---|---|---|---|
| 0.8 | 1.495 | 9.7 | 0.307 | 1.34 |
| 1.2 | 2.02 | 8.9 | 0.338 | 1.85 |
| 1.5 | 2.18 | 8.4 | 0.329 | 2.10 |
| 1.8 | 2.17 | 7.6 | 0.291 | 2.10 |
| 2.1 | 1.929 | 7.0 | 0.267 | 2.12 |
| 2.5 | 1.500 | 6.0 | 0.208 | 1.85 |

[a] Experimental data taken from S. H. Morrell and J. Stern[7]. $f_c$ calculated from their relative volume at rupture data, assuming crystal density = 1.00, amorphous density = 0.91.
[b] $TS = (K/M) [(M/M_c) - 1 + 10^{-4} Mf_c] (f_c + \{1 - f_c\}\omega_a)$, with $K = 24,600$, $M = 500,000$ (number-average), and $\beta^2$ (see text) = $10^{-3}$.

in error by less than a factor of ten gives credence to the theory, particularly when a variation of the parameters well within their reasonable physical limits reduces the error to an estimated factor of three.

A somewhat more direct test of the theory can be made using the data of Morrell and Stern[7], who report values for the tensile strength, length at break, and relative diminution in volume at break (from which the degree of crystallinity can be calculated) as a function of $1/M_c$ obtained from swelling measurements. A summary of their data and a comparison of the theoretical and experimental strengths are given in Table IV and Figure 8. The agreement between theory and experiment is fair.

### THE EFFECT OF TEMPERATURE

Only qualitative consideration can be given to the effect of temperature on strength, for $K$ as well as $f_c$ is temperature dependent. A graph of log $K$, calculated from the data of Table III, vs. $1/T$, the reciprocal absolute temperature, yields an "energy of activation" of about 3 to 4 kilocalories. This figure is small enough to be related to a fast reaction such as a chain transfer
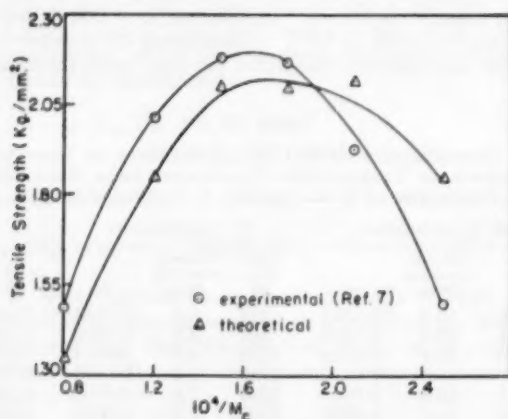


FIG. 8.—Tensile strength of natural rubber.

process, however, its significance is quite questionable.    The maximum in the strength of natural rubber at about $-17°$ C (Figure 5) is presumably due to its high rate of crystallization near this temperature.    Comparing Figures 4 and 5, it appears either that the maximum rate of crystallization of 5° C polybutadiene occurs at a much lower temperature than does that of natural rubber, or that its maximum rate, at whatever temperature it occurs, is so great that it cannot be supercooled, or at least was not supercooled at the cooling rate obtained in our apparatus.    The increase in the strength of natural rubber above room temperature has been discussed by Flory[2].

## CONCLUSIONS

The theory of strength proposed above appears to describe satisfactorily the effect of crosslinking on the strength of amorphous elastomers, and to apply semiquantitatively to crystallizable elastomers.    Further work, involving the effect of primary molecular weight, constitution, swelling, and additives is required to substantiate the general applicability of the theory.    The mechanism of rupture, in particular, is poorly understood.

## SYNOPSIS

The tensile strength of decamethylene dismethylazodicarboxylate vulcanizates of GR-S, 50° C polybutadiene, 5° C polybutadiene, and natural rubber has been determined as a function of temperature and/or the degree of crosslinking.    A theory of tensile strength of amorphous polymers which adequately describes the effect of the degree of crosslinking on strength is proposed.    The theoretical expression for the strength of amorphous materials is then modified to include the effect of crystallization.    The complete expression for the tensile strength of crystallizable elastomers, which includes amorphous elastomers as a special case, is:

$$TS = (K/M)[(M/M_c) - 1 + 10^{-4} Mf_c](f_c + \{1 - f_c\}\omega_0)$$

where $\omega_0 = 1 - (1 + \delta^2\lambda^2)^{-\frac{1}{2}}$, $f_c$ = volume fraction crystallinity, $M$ = primary molecular weight, $M_c$ = molecular weight per crosslink in the uncrystallized polymer, $\lambda$ = extension ratio at break, and $\delta$, $K$ = parameters.    The theory is shown to be good for GR-S and semiquantitatively correct for a crystallizable polymer, 5° C polybutadiene.

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# BEHAVIOR OF "PURE GUM" RUBBER VULCANIZATES IN TENSION *

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## INTRODUCTION

The state of vulcanization of rubber compounds usually has been determined from stress-strain measurements at some arbitrary load or elongation. Roth and Stiehler[1] found that the elongation $E$ of rubber under a fixed load changes with the time of cure $t$ in accordance with the equation:

$$(E - E_\infty)(t - t_0)k = 1 \tag{1}$$

where $E_\infty$, $t_0$, and $k$ are called vulcanization parameters. More recently, they have found[2] that the reciprocal of stress $F$ at a fixed elongation is related to the time of cure by a similar equation:

$$(F^{-1} - E_\infty^{-1})(t - t_0)k' = 1 \tag{2}$$

Unfortunately, the values of vulcanization parameters calculated from such equations were dependent on the load or elongation used and on the period of creep or stress relaxation preceding the measurement. The present study on the elongations of rubber vulcanizates under constant tensile loads was undertaken in an attempt to find some method of determining vulcanization parameters that would be independent of the conditions of test. The work reported here was limited to compounds of Hevea, GR-S, GR-I, and neoprene rubbers containing only antioxidants and ingredients necessary for vulcanization.

## EXPERIMENTAL PROCEDURE

The formulas and curing conditions given in Table I were employed for obtaining the data presented here. Where applicable, compounding and curing procedures given in ASTM Designation D15-52T[3] were followed. Strip specimens[4] approximately 0.65 cm. wide and 15 cm. long were cut from standard sheets 15 by 15 by 0.2 cm. in dimensions. The thickness of each specimen was measured to the nearest 0.01 mm. and bench marks $100.0 \pm 0.1$ mm. apart were placed on it. The specimens were then hung vertically, supporting fixed loads, and allowed to remain for periods up to 10,000 minutes. In most cases the periods were limited to about 1400 minutes. The loads used produced stresses of approximately 0.5, 1, 2, 3, 4, 5, 6, and 7 kg. per cm.$^2$. The exact stress on each specimen was calculated from the load and cross sectional area of the unstretched specimen. It is estimated that this calculated stress is accurate to within 1 per cent. The distance between bench marks was measured

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TABLE I

DESCRIPTION OF VULCANIZATES

| Type of rubber<br>Ingredients—parts by weight | Hevea | GR-S | GR-I | Neoprene |
|---|---|---|---|---|
| Rubber | 100 | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 | 5 |
| Magnesium oxide | — | — | — | 4 |
| Stearic acid | 1 | 1 | 1 | — |
| Sulfur | 2.5 | 2 | 2 | — |
| Mercaptobenzothiazole | 1 | 1 | — | — |
| Tetramethylthiuram disulfide | — | — | 1 | — |
| Phenyl naphthylamine | 1 | — | — | 1 |
| 2-Mercapto-imidazoline | — | — | — | 0.35 |

Cure:

| | Hevea | GR-S | GR-I | Neoprene |
|---|---|---|---|---|
| Temperature — ° C | 110 | 130 | 140 | 135 |
| Time—minutes | 20 | 20 | 20 | 20 |
| | 22 | — | 22 | — |
| | 25 | 25 | 25 | — |
| | 30 | 30 | 30 | — |
| | 40 | 40 | 40 | 40 |
| | 60 | 60 | 60 | — |
| | 80 | 80 | 80 | 90 |
| | 100 | 100 | 100 | — |
| | 120 | 120 | 120 | — |
| | — | 160 | 160 | — |
| | 240 | 240 | 240 | — |

1 minute after the load was applied and at suitable intervals thereafter using a cathetometer reading to 0.1 mm.

At the end of the creep measurements the loads were removed and the specimens were allowed to recover. In a few instances the recovery was followed from 1 minute to 1400 minutes after the load was removed in the same manner as the creep; but usually the specimens were placed in an oven for 30 minutes at a temperature about 30° C below the vulcanization temperature given in Table I in order to speed up the recovery.

Most of the measurements were made with an ambient temperature of 25° C. However, experiments were conducted in which the specimens and weights were enclosed in a housing with a plate glass window and maintained at 40° or 55° C. The temperature variation was about ±1° C during these tests. In one experiment the specimens were allowed to creep about 30 minutes at 70° C, then cooled and allowed to creep at 25° C.

## CREEP UNDER CONSTANT TENSILE LOAD

One of the initial purposes of the present study was to develop a practical procedure for deriving stress-strain relationships under conditions approaching equilibrium[5,6]. However, it was found that at 25° C even the most highly cured vulcanizates of all four rubbers continued to creep for 10,000 minutes under stresses ranging from 0.5 to 7 kg. per cm.$^2$, as illustrated in Figure 1. In those instances in which the elongation did not increase linearly with the logarithm of time, the slope increased, presumably because of degradation. The creep of well-cured specimens under small loads was very small. In such cases the elongation might mistakenly have been assumed to be constant, particularly if plotted on a linear time scale.
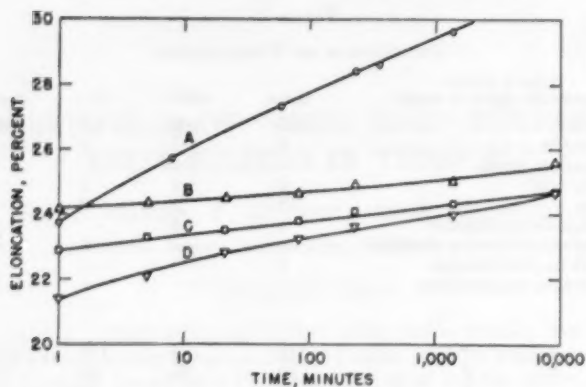
Fig. 1.—Typical creep curves at 25° C.

|        |          | Cure |          |          |
|--------|----------|------|----------|----------|
|        |          | Time, minutes | Tempera-ture, ° C | Stress, kg./cm.² |
| Curve  | Rubber   |      |          |          |
| A      | Neoprene | 90   | 135      | 2.97     |
| B      | Hevea    | 240  | 110      | 3.02     |
| C      | GR-I     | 240  | 140      | 2.03     |
| D      | GR-S     | 240  | 130      | 3.02     |

Since equilibrium was not attained in 10,000 minutes at 25° C, experiments were conducted at temperatures of 40° and 55° C. Between 1 and 1000 minutes the amount of creep was smaller at the higher temperatures, but there was no tendency for the elongation to approach a constant value. In fact, after 1000 minutes, the creep frequently increased at the higher temperatures as shown by the slope of the 55° C curve in Figure 2. In these instances recovery after the load was removed was not complete, indicating that flow (probably from degradation) had occurred. This behavior was especially noticeable for
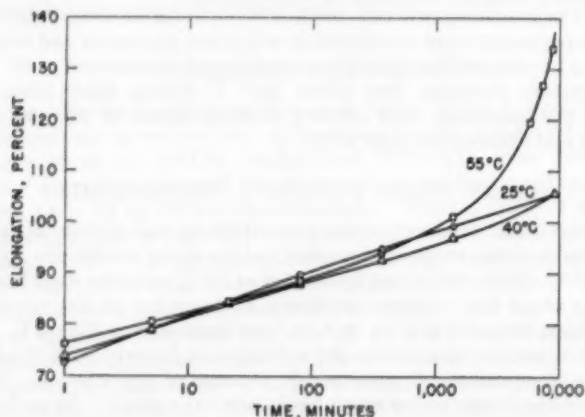


Fig. 2.—Creep of GR-I vulcanizates at temperatures of 25°, 40° and 55° C. The cure was 30 minutes at 140° C and the stress was about 3 kg. per cm.²

undercured specimens supporting large loads.    In an attempt to eliminate the increased creep after long times at high temperatures, an experiment was conducted in which the specimens were allowed to creep under a load of 3 kg. per cm.² for about 30 minutes at 70° C, followed by creep at 25° C.    The elongation still increased linearly with the logarithm of time.

Because there was no advantage in working at higher temperatures most of the measurements were made at 25° C.    Also, most of the experiments were terminated after 1400 minutes.    The ratio

$$[E_{1000} - E_{10}]/[E_{100} (\log 1000 - \log 10)]$$

## TABLE II

### CREEP OF RUBBER VULCANIZATES*

| Cure, min. | Stress, kg./cm.² | Rubber | | | |
|---|---|---|---|---|---|
| | | Hevea | GR-S | GR-I | Neoprene |
| 20 | 1 | 0.073 | 0.191 | 0.113 | 0.142 |
| | 2 | 0.100 | 0.255 | 0.142 | 0.187 |
| | 3 | 0.125 | 0.288 | 0.153 | 0.225 |
| 30 | 1 | 0.034 | 0.118 | 0.085 | — |
| | 2 | 0.460 | 0.144 | 0.069 | — |
| | 3 | 0.054 | 0.180 | 0.092 | — |
| | 4 | 0.065 | 0.178 | 0.083 | — |
| 40 | 1 | 0.027 | 0.086 | 0.044 | 0.070 |
| | 2 | 0.025 | 0.099 | 0.051 | 0.084 |
| | 3 | 0.036 | 0.111 | 0.064 | 0.099 |
| | 4 | 0.040 | 0.124 | 0.064 | 0.115 |
| 60 | 1 | 0.012 | 0.052 | 0.035 | — |
| | 2 | 0.013 | 0.061 | 0.034 | — |
| | 3 | 0.025 | 0.071 | 0.041 | — |
| | 4 | 0.028 | 0.069 | 0.048 | — |
| | 5 | 0.021 | 0.105 | 0.045 | — |
| 80 | 1 | 0.014 | 0.032 | 0.025 | 0.045† |
| | 2 | 0.015 | 0.054 | 0.027 | 0.054† |
| | 3 | 0.018 | 0.052 | 0.031 | 0.064† |
| | 4 | 0.022 | 0.055 | 0.038 | 0.074† |
| | 5 | 0.014 | 0.079 | 0.038 | 0.084† |
| 240 | 1 | 0.007 | 0.023 | 0.014 | — |
| | 2 | 0.013 | 0.035 | 0.017 | — |
| | 3 | 0.010 | 0.040 | 0.018 | — |
| | 4 | — | 0.045 | 0.018 | — |
| | 5 | 0.013 | 0.044 | 0.021 | — |

* The values in the table represent the increase in elongation from 10 to 1000 minutes divided by twice the elongation at 100 minutes; i.e., $E_{1000} - E_{10}/2E_{100}$.
† Cured 90 minutes.

was determined for each specimen.    These ratios, given in Table II, usually decreased with increasing time of cure and increased with the load.    Hevea had the lowest and GR-S and Neoprene the highest ratios.

Studies of recovery of the specimens after they had been allowed to creep for about 1400 minutes at 25° C indicated that the creep was essentially recovered as can be seen in Figure 3.    It was possible to obtain recovery more quickly by heating the specimens for 30 minutes at a temperature 30° C below the vulcanization temperature, so most recovery measurements were made in
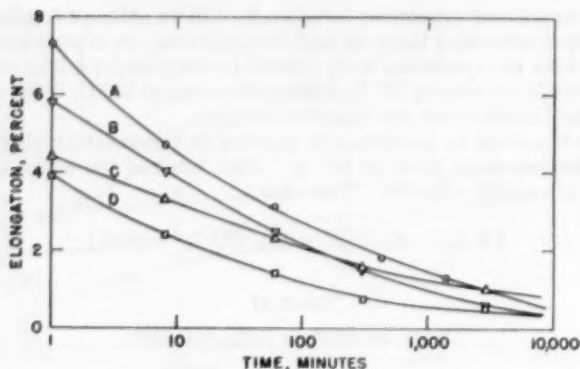
Fig. 3.—Typical recovery curves after 1400 minutes creep.  The cure time was 40 minutes.

| Curve | Rubber | Elongation at end of creep period, % | Stress during creep period, kg./cm.$^2$ |
|-------|--------|--------------------------------------|-----------------------------------------|
| A | Neoprene | 38.7 | 3.0 |
| B | GR-S | 29.0 | 2.0 |
| C | Hevea | 35.6 | 2.0 |
| D | GR-I | 38.2 | 2.0 |

this manner.  It was found that such treatment had no adverse effect on the vulcanizates.

Lastly, the behavior of rubber vulcanizates under load after prestressing at twice the load was examined.  Specimens were subjected to a load of 4 kg. per cm.$^2$ for 24 hours.  The load was then reduced to 2 kg. per cm.$^2$ on some specimens.  Other specimens were allowed to recover under zero load for 5 minutes before applying the load of 2 kg. per cm.$^2$  As can be seen in Figure 4, the behavior was complicated.  Recovery and creep occurred simultaneously, over a period at least as long as the period of initial prestressing.  The exact behavior depended on the previous history of the specimen.  With the prestressed specimens, a minimum elongation was reached in about 24 hours; then, after about 48 hours creep became predominant.  Since elongation after prestressing was sensitive to the history of the specimen, our study was restricted to specimens that had not been previously strained.

These results indicate that equilibrium can not be reached in a reasonable time at temperatures up to 70° C.  Since the creep was found to be essentially recoverable, this failure to attain an equilibrium state can not be ascribed to flow or degradation phenomena.  These findings are in agreement with those of Wildschut[7] and Gehman[8].  Accordingly, there appears to be no practical way of measuring the stress-strain properties of rubber vulcanizates under equilibrium conditions.

## STRESS-STRAIN RELATIONSHIP

Since the stress-strain relationship could not be measured under equilibrium conditions, it appeared that the best procedure was to determine the relationship for specimens that had been allowed to creep for a fixed period.  Elongations for vulcanizates of Hevea, GR-S, GR-I, and neoprene were determined for specific periods of creep.  The different points on a given stress-strain curve were obtained by using a number of specimens cut from the same sheet and
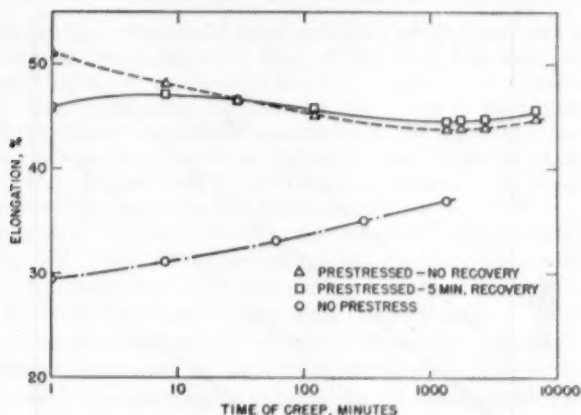
FIG. 4.—Influence of prestressing on creep of Hevea vulcanizate.  Temperature 25° C.
Prestress load 4 kg. per cm.²; creep load 2 kg. per cm.²

applying a different load to each specimen.    Each level of cure given in Table I
was investigated.

The experimental stress-strain curves could not be represented by either of
the theoretical stress-strain functions thus far advanced[9].    Therefore, an empiri-
cal approach was used to ascertain whether a single function could represent
all of the curves.    It was found by graphical methods that all the stress-strain
curves were similar up to about 200 per cent elongation.    In other words, it was
possible to represent all the experimental data by one form of stress-strain curve,
if each stress $F$ for a vulcanizate was multiplied by a constant characterizing
that vulcanizate.    This constant was chosen to be the reciprocal of the modu-
lus $M$, where $M$ is the slope of the stress-strain curve at the origin.

To estimate the values of $M$, the data obtained at elongations from 3 to 100
per cent was extrapolated.    In a few cases values of $M$ were determined from
measurements of elongations of a few tenths of a per cent with a microscope
comparator.    The stresses for these elongations were between 0.01 and 0.1 kg.
per cm.² and Hooke's Law based on actual cross section was assumed to be
valid.    The values of $M$ obtained in this way were in agreement with those
extrapolated from the higher elongations.

Although graphical extrapolations were used initially, it was found more
satisfactory to use empirical mathematical relationships for this purpose.    The
following equation was found to represent the data very well for elongations up
to about 200 per cent:

$$F = M(L^{-1} - L^{-2}) \exp A(L - L^{-1}) \tag{3}$$

where $A$ is a parameter whose value changes only slightly with the time of creep
and the time of cure and $L$ is the ratio of the extended length to the original
length.    $L$ is related to the elongation in per cent by the equation:

$$E = 100(L - 1). \tag{4}$$

If Equation (3) is valid, a plot of $\log F/(L^{-1} - L^{-2})$ vs. $(L - L^{-1})$ should
be a straight line.    Such plots were linear as illustrated in Figure 5.    The
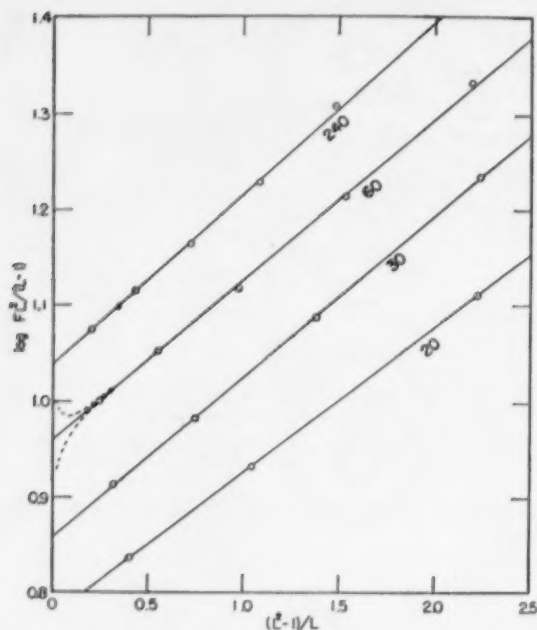
Fig. 5.—Stress-strain relationship for GR-I vulcanizates after 100 minutes creep. The numerals indicate the cure in minutes. The broken lines indicate the precision of measurement.

dotted lines indicate the limits for an error of $\pm 0.001$ in the measurement of $L$. From these plots, the values of $A$ were calculated from the slopes and the values of $M$ from the intercepts when $(L - L^{-1})$ is equal to zero (i.e., $L = 1$ or $E = 0$). Table III lists the values of $A$. It is seen that these values tend to increase slightly with an increase in either the time of creep or the time of cure. This increase is greatest for GR-I and least for Hevea vulcanizates. Table IV gives the values of the modulus $M$ for vulcanizates of the four rubbers. As expected, the values decrease with an increase in time of creep and increase with an increase in time of cure.

Other rubber compounds were tested and the data plotted in the manner shown in Figure 5. "Pure gum" compounds, including those consisting of 100 parts Hevea and 8 parts of sulfur, were found to give linear plots in the region of the stress-strain curve in which there was no appreciable crystallization or flow. Therefore it appeared that Equation (3) is applicable for all "pure gum" compounds. Further work since this paper was submitted for publication has shown that the form of the stress-strain relationship for "pure gum" vulcanizates depends on the temperature and that Equation (3) for elongations below 50% ($L < 1.5$) applies only for a limited temperature range. Equation (3) has been found to apply over some temperature range for every "pure gum" vulcanizate investigated. On the other hand, compounds containing carbon black or other fillers did not give linear plots indicating that Equation (3) does not represent their stress-strain properties.

## COMPARISON WITH OTHER STRESS–STRAIN RELATIONSHIPS

The form of the stress-strain relationship for rubber has been the subject of many previous investigations[9]. Most of this work has been related either to a supposed "equilibrium" curve or to a curve obtained at a fixed rate of grip separation. The relationship in Equation (3) refers to the values obtained after specific periods of creep under contant load. It is probable that this relationship also can be used for values obtained after a specific period of stress relaxation. Data of Roth and Wood[10] for the stress in a GR-S compound after about 2 hours of relaxation confirm this supposition.

A comparison of Equation (3) with other stress-strain relationships is shown in Figure 6. All of the curves are normalized by using for the ordinate the ratio $F/M$. Thus, the curves all have a slope of unity at the origin. Curve A represents Hooke's Law based on the cross sectional area of the unstretched specimen, curve B the statistical or kinetic theory of rubberlike elasticity, curve C Hooke's Law based on the cross sectional area of the stretched specimen, and curve D the relationship of Equation (3), using 0.38 for the value of A.

### TABLE III

#### VALUES FOR "$A$" IN EQUATION (3)

| Rubber | Minutes of cure | Time of creep in minutes | | | |
|---|---|---|---|---|---|
| | | 1 | 10 | 100 | 1000 |
| Hevea | 20 | 0.35 | 0.36 | 0.36 | 0.37 |
| | 22 | 0.35 | 0.36 | 0.36 | 0.37 |
| | 25 | 0.35 | 0.36 | 0.36 | 0.37 |
| | 30 | 0.36 | 0.37 | 0.36 | 0.37 |
| | 40 | 0.36 | 0.37 | 0.37 | 0.37 |
| | 60 | 0.36 | 0.37 | 0.37 | 0.37 |
| | 80 | 0.36 | 0.36 | 0.37 | 0.37 |
| | 100 | 0.36 | 0.37 | 0.38 | 0.38 |
| | 120 | 0.36 | 0.37 | 0.38 | 0.38 |
| | 240 | 0.36 | 0.37 | 0.37 | 0.38 |
| GR-S | 20 | 0.33 | 0.33 | 0.34 | 0.36 |
| | 25 | 0.34 | 0.34 | 0.35 | 0.37 |
| | 30 | 0.34 | 0.34 | 0.35 | 0.38 |
| | 40 | 0.35 | 0.35 | 0.36 | 0.38 |
| | 60 | 0.35 | 0.36 | 0.36 | 0.38 |
| | 80 | 0.35 | 0.37 | 0.37 | 0.38 |
| | 100 | 0.36 | 0.37 | 0.37 | 0.38 |
| | 120 | 0.36 | 0.37 | 0.37 | 0.38 |
| | 160 | 0.36 | 0.37 | 0.37 | 0.38 |
| | 240 | 0.36 | 0.37 | 0.37 | 0.38 |
| GR-I | 20 | 0.32 | 0.33 | 0.34 | 0.36 |
| | 22 | 0.33 | 0.34 | 0.36 | 0.37 |
| | 25 | 0.34 | 0.36 | 0.37 | 0.38 |
| | 30 | 0.36 | 0.37 | 0.38 | 0.39 |
| | 40 | 0.37 | 0.38 | 0.38 | 0.39 |
| | 60 | 0.38 | 0.38 | 0.39 | 0.40 |
| | 80 | 0.39 | 0.40 | 0.40 | 0.40 |
| | 100 | 0.39 | 0.40 | 0.40 | 0.41 |
| | 160 | 0.40 | 0.40 | 0.41 | 0.40 |
| | 240 | 0.40 | 0.41 | 0.41 | 0.42 |
| Neoprene | 20 | 0.38 | 0.38 | 0.38 | 0.39 |
| | 40 | 0.38 | 0.38 | 0.39 | 0.40 |
| | 90 | 0.38 | 0.39 | 0.39 | 0.40 |

TABLE IV

VALUES FOR MODULUS "M"

| Rubber | Time of cure, minutes | Time of creep in minutes | | | |
|---|---|---|---|---|---|
| | | 1 kg./cm.³ | 10 kg./cm.³ | 100 kg./cm.³ | 1000 kg./cm.³ |
| Hevea | 20 | 8.5 | 7.9 | 7.5 | 7.0 |
| | 22 | 9.1 | 8.6 | 8.2 | 7.7 |
| | 25 | 9.7 | 9.3 | 9.0 | 8.6 |
| | 30 | 10.7 | 10.3 | 10.1 | 9.7 |
| | 40 | 12.2 | 11.9 | 11.8 | 11.5 |
| | 60 | 13.9 | 13.7 | 13.5 | 13.3 |
| | 80 | 15.0 | 14.8 | 14.6 | 14.4 |
| | 100 | 15.6 | 15.4 | 15.2 | 15.0 |
| | 120 | 16.1 | 15.9 | 15.6 | 15.5 |
| | 240 | 16.5 | 16.2 | 16.2 | 16.0 |
| GR-S | 20 | 8.9 | 7.5 | 6.4 | 5.6 |
| | 25 | 10.0 | 8.7 | 7.7 | 6.8 |
| | 30 | 10.9 | 9.7 | 8.7 | 7.8 |
| | 40 | 12.4 | 11.3 | 10.4 | 9.7 |
| | 60 | 14.5 | 13.4 | 12.7 | 12.0 |
| | 80 | 15.6 | 14.7 | 14.1 | 13.4 |
| | 100 | 16.3 | 15.5 | 15.0 | 14.2 |
| | 120 | 16.9 | 16.2 | 15.7 | 15.0 |
| | 160 | 17.6 | 16.9 | 16.4 | 15.8 |
| | 240 | 17.9 | 17.2 | 16.7 | 16.2 |
| GR-I | 20 | 7.5 | 6.6 | 6.0 | 5.5 |
| | 22 | 7.7 | 6.8 | 6.3 | 5.8 |
| | 25 | 8.0 | 7.2 | 6.7 | 6.3 |
| | 30 | 8.4 | 7.7 | 7.3 | 6.9 |
| | 40 | 9.0 | 8.5 | 8.2 | 7.8 |
| | 60 | 9.8 | 9.4 | 9.1 | 8.8 |
| | 80 | 10.3 | 9.9 | 9.7 | 9.5 |
| | 100 | 10.6 | 10.2 | 10.0 | 9.8 |
| | 160 | 11.1 | 10.8 | 10.6 | 10.6 |
| | 240 | 11.4 | 11.1 | 10.9 | 10.8 |
| Neoprene | 20 | 11.8 | 9.9 | 8.6 | 7.6 |
| | 40 | 14.4 | 13.1 | 12.2 | 11.4 |
| | 90 | 16.2 | 15.1 | 14.4 | 13.7 |

The statistical (kinetic) theory of rubberlike elasticity predicts that the equilibrium stress should be proportional to $L - L^{-2}$. It can be seen in Figure 6 that the actual stress-strain curve represented by curve D lies considerably below that predicted by the statistical theory. Further, the shape of curve B is such that it can not be made to agree with the experimental data by varying the apparent modulus $M$, and the deviation of curve B from curve D is evident even at low elongations. Other observers have noted this deviation and Treloar[11] states that its cause is not at all well understood.

Mooney and Rivlin[9,12,13,14] have developed a general strain-energy function for rubber which in the case of extension reduces to the following equation:

$$F/2(L - L^{-2}) = C_1 + C_2 L^{-1} \tag{5}$$

where $C_1$ and $C_2$ are constants for a particular vulcanizate. Values of $F/M$ and $L$ obtained from our data were used to determine the variables plotted as coordinates in Figure 7, as suggested by Equation (5). Since a straight line was not obtained, it was concluded that Equation (5) does not represent the stress-strain behavior of rubber. Thomas[15] noted deviations from Equation
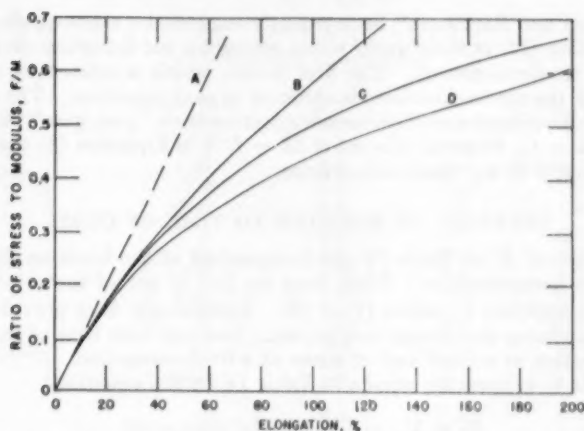
Fig. 6.—Comparison of various relationships between $F/M$ and elongation. A. Hooke's Law on original cross section: $F/M = L - 1$. B. Kinetic Theory: $F/M = (L - L^{-2})/3$. C. Hooke's Law on actual cross section: $F/M = 1 - L^{-1}$. D. Empirical relationship: $F/M = (L^{-1} - L^{-2})$ exp $0.38$ $(L - L^{-1})$.

(5) similar to those indicated by Figure 7 and he proposed another stress-strain relationship. It also does not satisfactorily represent the behavior of rubber.

If the exponential term in Equation (3) is replaced by $L$, Hooke's Law for stress measured on the stressed section (Curve C in Figure 6) is obtained. This equation has been suggested by several previous workers, and it does approximate the data reasonably well for elongations below 10 per cent. If the exponential term in Equation (3) is replaced by the first two terms of its expansion $(1 + 2\ AE)$, the stress-strain curve is approximated up to about 100 per cent elongation.
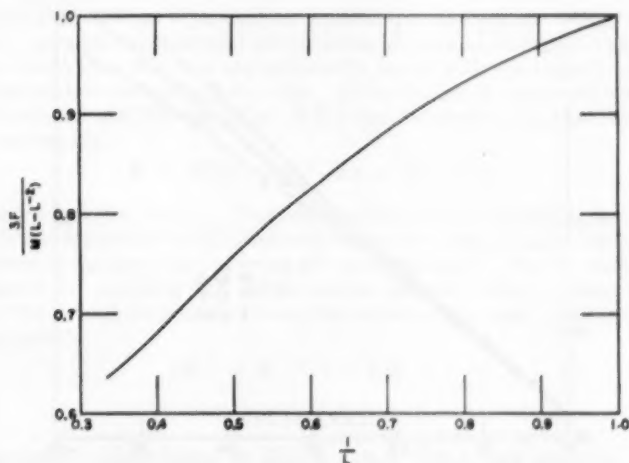


Fig. 7.—Normalized stress-strain relationship for rubber using the variables in Equation 5 for coordinates.

Blanchard and Parkinson[16] have recently suggested a stress-strain relationship (Equation (12) in their work) which resembles our Equation (3) and gave impetus to its development. The first factor, which is related to the stress measured on the stressed section, is identical in each equation. The exponential term in Blanchard and Parkinson's equation for a "pure gum" vulcanizate is exp $0.5 (L - 1)$; whereas, it is exp $A (L - L^{-1})$ in Equation (3) the value of $A$ being about 0.38 for most vulcanizates.

### RELATION OF MODULUS TO TIME OF CURE

The values of $M$ in Table IV are independent of the loads or elongations used in their determination. Thus, they are free of one of the objections encountered in applying Equation (1) or (2). Accordingly, they provide a better basis for examining the change in a physical property with time of cure $t$, than either elongation at a fixed load or stress at a fixed elongation.

Attempts to express the results in Table IV by the equation:

$$M = M_\infty - (M_\infty - M_0) \exp (- kt) \qquad (6)$$

which is similar to that used by Gee and Morrell[17] (Equation (5) in their paper), were not successful. On the other hand, the results did conform with the following equation which is similar to Equation (2).

$$(M^{-1} - M_\infty^{-1})(t - t_0)k^0 = 1 \qquad (7)$$

This equation requires that $1/M$ be a linear function of $1/(t - t_0)$. It is seen in Figure 8 that a linear relationship is obtained if the proper value of $t_0$ is selected. All the compounds listed in Table IV give similar plots for each time of creep.

The parameters $M_\infty$ and $k^0$ can be determined respectively from the intercept and slope of plots like Figure 8. Table V lists the values so determined
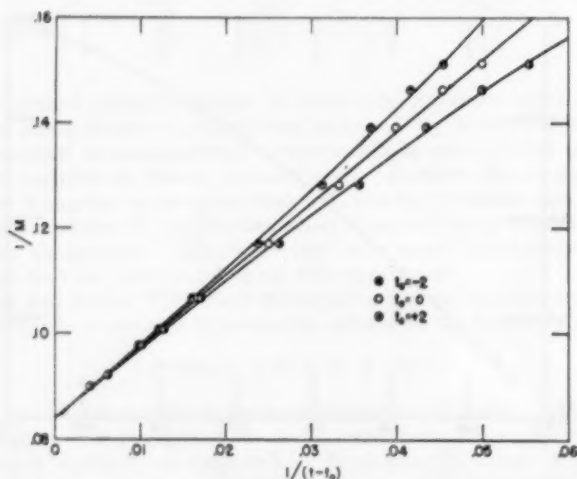


Fig. 8.—Relationship between modulus and time of cure for GR-I vulcanizates.

## TABLE V

### VULCANIZATION PARAMETERS

| Rubber | Creep time, minutes | $t_0$, minutes | $M_\infty$, kg./cm.$^2$ | $k^0$, kg./cm.$^2$ minutes |
|--------|---------|------|-------|--------|
| Hevea | 1 | 3.5 | 18.9 | 0.935 |
|  | 10 | 6.0 | 18.4 | 0.990 |
|  | 100 | 7.5 | 18.0 | 1.040 |
|  | 1000 | 9.0 | 17.9 | 1.040 |
| GR-S | 1 | 0.0 | 20.6 | 0.780 |
|  | 10 | 3.0 | 20.2 | 0.695 |
|  | 100 | 5.0 | 20.1 | 0.625 |
|  | 1000 | 7.0 | 19.4 | 0.580 |
| GR-I | 1 | −5.0 | 12.2 | 0.775 |
|  | 10 | 0.0 | 11.9 | 0.735 |
|  | 100 | 3.0 | 11.7 | 0.725 |
|  | 1000 | 4.5 | 11.6 | 0.670 |
| Neoprene | 1 | 2.5 | 17.9 | 2.00 |
|  | 10 | 6.5 | 16.8 | 1.75 |
|  | 100 | 8.0 | 16.5 | 1.52 |
|  | 1000 | 9.0 | 15.7 | 1.34 |

for the three parameters for each compound at each time of creep. It is seen that the time of creep has a pronounced effect on the parameters, particularly $t_0$. At the shortest creep time, $t_0$ is negative in one instance. Negative values of $t_0$ have been noted previously in the application of Equations (1) and (2), and were attributed to crystallization or prevulcanization effects[1,2]. These effects were undoubtedly responsible for some of the negative values noted for $t_0$. However, other negative values could not be ascribed to either of these effects, and it now appears that the short time of creep (1 minute) was responsible.

## CONCLUSION

No practical method of measuring equilibrium stress-strain values could be developed, because experimental observations showed an increase in elongation under constant load that was approximately linear with the logarithm of time unless degradation became appreciable. Nevertheless, it was found that "pure gum" vulcanizates of Hevea, GR-S, GR-I and neoprene have the same stress-strain relationship,

$$F = M(L^{-1} - L^{-2}) \exp A(L - L^{-1})$$

for any fixed period of creep. This relationship was used to determine a modulus which is independent of the load or elongation employed, although its value does depend upon the period of creep or relaxation used. Such a modulus was found useful for studying the vulcanization characteristics of these rubbers. Values of the modulus calculated for all the vulcanizates were found to conform to the equation

$$(M^{-1} - M_\infty^{-1})(t - t_0)k^0 = 1$$

## SUMMARY

"Pure gum" vulcanizates of Hevea, GR-S, GR-I, and neoprene rubbers were subjected to constant tensile loads. Their elongations were measured to the nearest 0.1 per cent at intervals of time from 1 to 10,000 minutes. For

temperatures between 25° and 55° C the elongations in most cases increased approximately linearly with the logarithm of time. The stress-strain curves after a given period of creep could not be represented by any of several published relationships. However, the curves for all vulcanizates were similar up to about 200 per cent elongation and could be represented by the empirical equation:

$$F = M(L^{-1} - L^{-2}) \exp A(L - L^{-1})$$

where $F$ is the stress based on the original cross sectional area, $L$ is the extension ratio, $M$ is Young's modulus, and $A$ is a constant, equal to approximately 0.38. The moduli $M$ were calculated for all the vulcanizates using several periods of creep and found to conform to the equation:

$$(M^{-1} - M_\infty^{-1})(t - t_0)k^0 = 1$$

where $t$ is the time of cure, and $M_\infty$, $t_0$, and $k^0$ are vulcanization parameters.

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# HELICAL SPRING STRESS RELAXOMETER *

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Changes in the tensile properties of rubber are obviously of great practical importance. Consequently, measurements of the change in force required to maintain or produce a given extension under controlled conditions of temperature and atmosphere have frequently been made and have advanced our understanding of the physical process of crystallization[1] and of the chemical reactions responsible for thermal aging[2,3] to the extent that they may become routine test procedures.

The decrease in the force required to maintain a constant extension during the period of aging (stress relaxation) has been the most common measurement, in part because rubber elasticity theory predicts an equality between the fractional decrease in force and the fraction of the network chains originally supporting the stress which have become ineffective[2]. Stress-relaxation behavior may characterize the type of scission reaction occurring; for example, the stress relaxation of most vulcanizates can be interpreted as a first-order scission of crosslinks, and not as a random scission of monomeric units in the chains between crosslinks[3].

Stress-relaxation results, however, do not provide all the necessary information on network changes—the final properties of the rubber depend not only on crosslink or chain scission but to a comparable degree on crosslink formation during aging, which does not affect the force at constant extension[4]. To examine this second effect requires measurements on the intermittent stretching of an unstrained sample to a constant extension.

Parallel measurements of force at constant and intermittent extension under identical aging conditions are therefore required. The several designs of apparatus already described have usually been rather complicated and require practice and skill in use. A simple apparatus developed in these laboratories, which can readily be used for routine operations, is described in the following paragraphs. The fractional change in force is read directly from a vernier scale on the instrument, and may be immediately plotted on a force-time graph, preferably as $\log_{10}$ (force/force$_{t=0}$) vs. time (cf. Reference 3).

## THE CONTINUOUS STRESS RELAXOMETER

The main part of the apparatus consists of a slotted bar AB, shown in Figure 1a. The position of the block D on AB is controlled by rotation of the lead screw (via the slotted head C) which is fitted into the longitudinal slot in the bar, passing through the tapped hole in D. To the block is attached the upper end of a helical steel spring from the lower end of which is suspended, through a swivel, the upper specimen clamp E. The swivel is necessary for adjustment of the position of E so that it is parallel to the bar. From the front of the adjust-

Glass tube

Spring

Section through G

Figure Ib

Helical spring

G

Specimen

Brass turnkey

Glass tube

Cork

Rivet

Tufnol blade

Figure Ic

1 cm
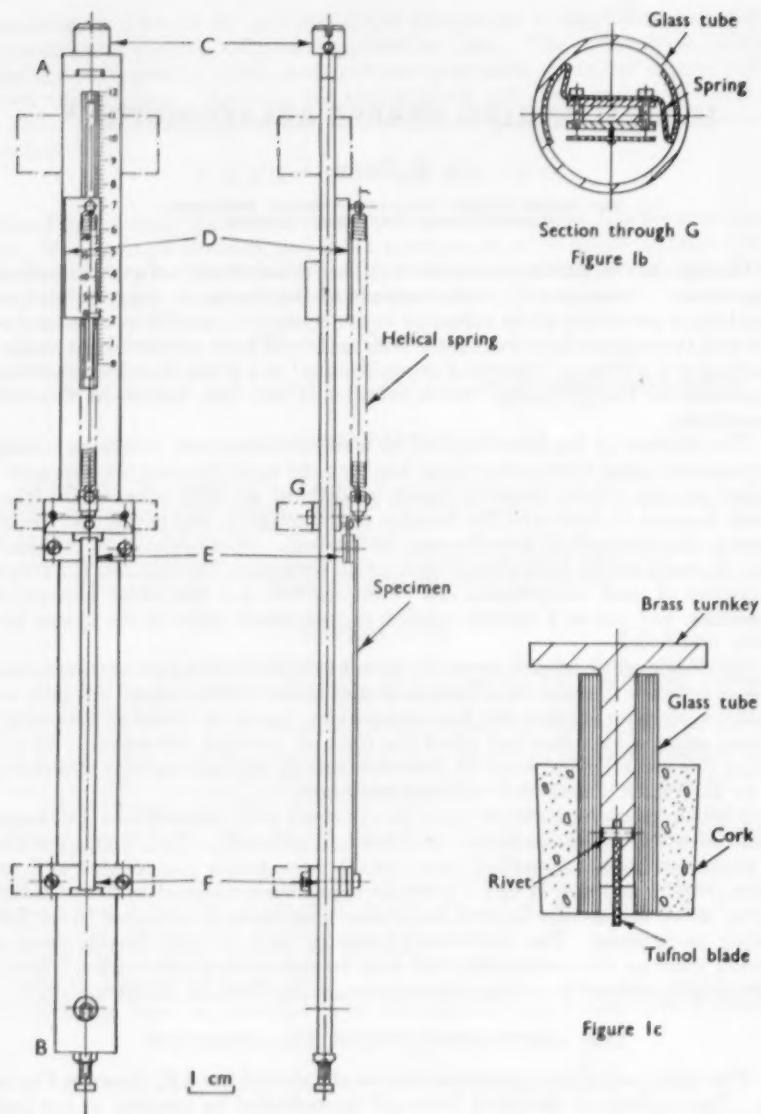
Figure Ia

able stop G, which is clamped on AB, protrudes a pin which passes through a clearance hole in E, and so limits its movement relative to the bar.   The position of the lower specimen clamp F on AB is adjusted to give the sample its desired extension, maintained constant throughout the experiment by the stop

G which also prevents spring recoil should the sample rupture. A linear (arbitrary) scale is engraved on AB so that the vernier scale on D indicates zero at its lowest point of travel.

The design of the specimen clamps will depend on the type of test piece adopted; the ones illustrated (Figure 1a) are for use with a strip specimen. A simple strip sample is economical of experimental material, and a suitable clamp for this type consists of two flat plates, the upper edge of the front one being radiused. The specimen is clamped between the plates by means of two screws, and then passes over the radiused edge to the other clamp where it is similarly held. Clamps have also been designed to hold T-50 type dumbbells. Stainless steel is used for both types of clamp.

The relaxometer is located centrally in a glass tube by means of three phosphor-bronze springs, illustrated in Figure 1b, which also serve as heat-conducting paths to the relaxometer from the walls of the containing vessel. To prevent vertical movement in the tube a screw and locknut adjustment is provided. For experiments in a closed system a special type of glass stopper is used (Figure 2). The turnkey K is inserted into the stopper so that the tungsten points engage in the 'slot in the head of the lead-screw C, which fits snugly into the base of the stopper. For work in air at atmospheric pressure, a simpler type of stopper may be used, consisting of a cork or wooden bung through the center of which passes a screw-driver blade (Figure 1c). For most processes it is essential that the temperature be maintained constant within fine limits to obtain satisfactory results, much better than is possible in an air oven. The glass vessel is therefore normally inserted into a liquid thermostat, fitted with a transparent window, through which the relaxometer is observed.

*Experimental materials.*—The samples may conveniently be molded or punched from a thin sheet of material. A T-50 dumbbell punch may be used, or for strip samples, a cutter of the type shown in Figure 3 is easily constructed. This design has the advantage that the cutting edges (single-edge razor blades) are readily replaced should they become blunted or chipped.

*Operation of the relaxometer.*—With the spring and the empty upper specimen clamp E in place, the apparatus is zeroed at the reaction temperature by bringing the block D to the lowest point of travel, i.e., to the zero of the engraved scale, and adjusting the position of the stop G so that the clamp E is just swinging free of the pin of G. The clamp is removed and the specimen inserted (for strip specimens a jig may be used). Bench marks are applied to the surface. The lower clamp F is then loosely attached to the bar, and the upper clamp resuspended from the spring. The lower clamp is adjusted to give the desired extension as indicated by the bench marks, and finally tightened. The screw thread is rotated until the clamp E is once again swinging free of the pin. The apparatus is then ready for use.

The tensile properties of the sample will determine the appropriate spring to be used for the study of its stress relaxation. It should be such that when the instrument is in adjustment at the reaction temperature, the block D is as near the top of AB as conveniently possible. This ensures maximum accuracy of the subsequent measurements. The provision of springs of varying stiffness, but approximately the same length enables a range of specimens of different moduli to be examined with the minimum of zero readjustment.

The relaxometer in its reaction vessel is placed in the thermostat, and when thermal equilibrium is attained, the balance point (when the forces exerted by the specimen and the spring are equal) is found by observation of the oscillation of the clamp E about the pin G, i.e., when it is lifted from the pin by the action
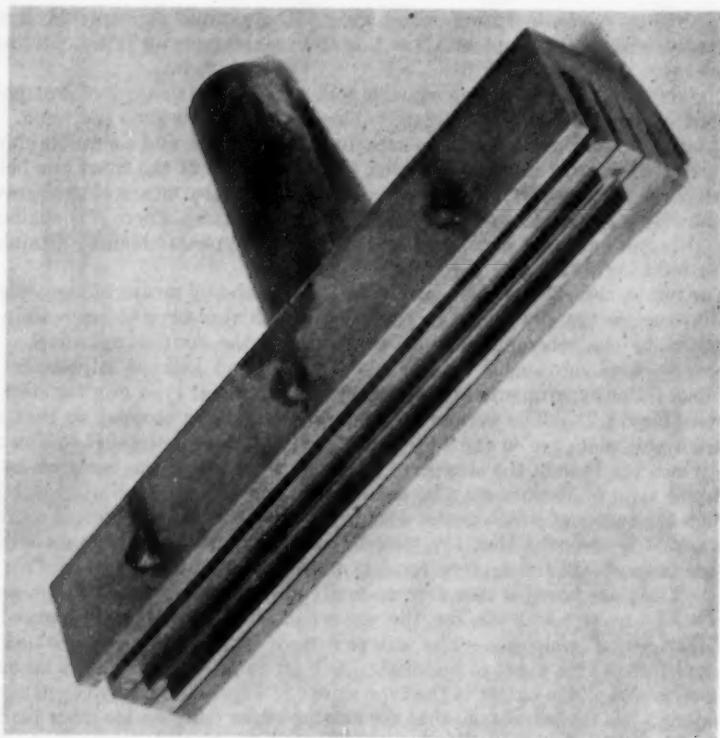
Fig. 3.
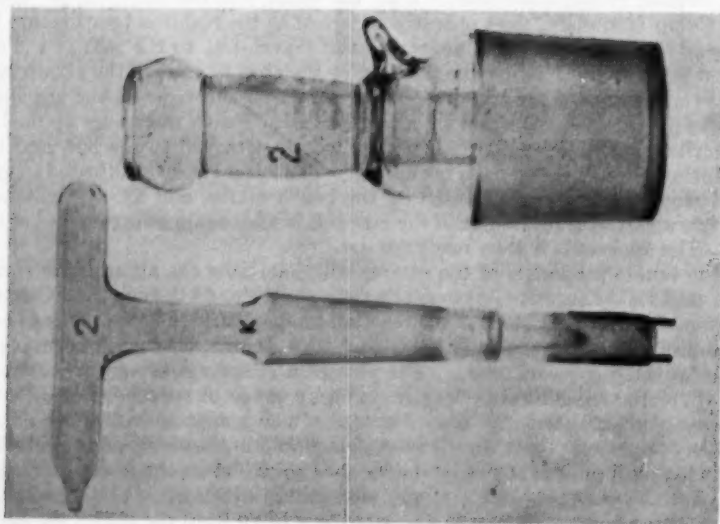


Fig. 2.
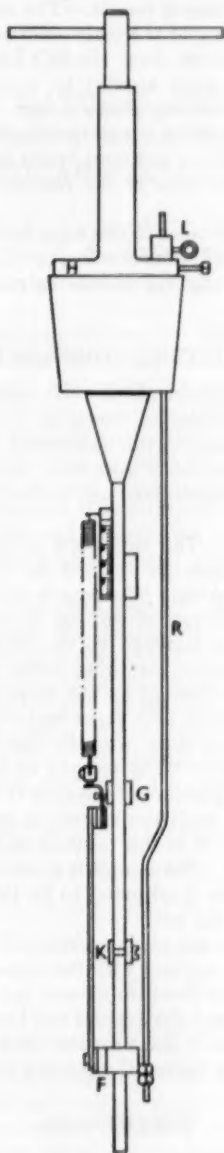
Fig. 4.

of the spring. This adjustment is, of course, carried out by rotation of the lead screw by the turnkey. The reading of the vernier is then taken, and the operation repeated at convenient time intervals.

*Calculation and representation of results.*—The zero adjustment of the relaxometer is such that the reading of the scale observed is directly proportional to the extension of the spring, which, since Hooke's Law is strictly obeyed, is itself directly proportional to the force applied to, and exerted by, the specimen. Plotting these readings on semi-log graph paper, or the logarithm or normal graph paper, against time, gives the characteristic stress relaxation curve. It is usual to bring all the curves to a common origin for comparative purposes by plotting the logarithm of the ratio of the reading at any time to the initial value.

One of the principle advantages in the experimental method given above is that calibration of the springs is unnecessary, provided that they obey Hooke's Law, and consequently the reading of the instrument taken is that used in representing the results.

## THE INTERMITTENT STRESS RELAXOMETER

The object of the intermittent stress relaxometer is to measure the force exerted by the sample at an extension constant in any single experiment, while maintaining it between readings in the unstrained state. This is achieved by controlling the position of the lower specimen clamp on the bar between the limits at which the sample is unstrained and at the extension at which the force is to be measured.

*Description of apparatus.*—The side view of the modified relaxometer is shown in Figure 4. The main bar is fixed to the bottom of the modified stopper by means of two brackets. The length of the operating screw-driver is increased to avoid fouling the end of the rod R controlling the movement of the lower clamp. The rod is fastened to the back plate of the clamp F and passes through the stopper and a clamping collar H. The movement of the clamp on the bar is therefore limited by the stops on the bar (K) and on the rod (L). A dumbbell cut from thin sheet material with a T-50 punch is the most suitable specimen for this work, and the clamp is designed accordingly.

*Operation of the relaxometer.*—The zeroing of the instrument is exactly as described above. When the position of the stop G has been adjusted the lower specimen clamp F is moved until the sample is just unstrained. The rod is locked by means of the collar H in this position and the stop K adjusted to fix the upper limit of movement. The sample is given its desired extension and the position of the clamping collar L adjusted to fix the lower limit of movement. The apparatus is then ready for use.

During the experiment the sample is maintained in the unstrained state, i.e., with the specimen clamp F in contact with the upper limiting stop K. To take a reading the clamp is pushed down to extend the sample the distance determined by the position of L, and the control rod locked by means of the clamp H. The reading is then taken in the way described previously for the continuous stress relaxometer. After taking the reading the sample is returned to the unstrained state.

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# BRANCHED CHAIN NATURAL RUBBER DERIVATIVES OBTAINED BY REACTION WITH AZODICARBOXYLATES *

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The azo group in esters of azodicarboxylic acid (HOOC—N=N—COHO) is very reactive with compounds which have active hydrogen atoms. Alder, Pascher, and Schmitz[1] showed that ethyl azodicarboxylate forms branched chain compounds with natural and synthetic rubbers. The ease with which azo compounds of this type combine with rubber shows that compounds containing two such active groups may be used for the formation of crosslinks. Such compounds are likely to be good vulcanizing agents. If so, they may be important for quantitative studies of vulcanization, since by their means it is possible to introduce a definite and controllable number of crosslinks between molecules of rubber or similarly unsaturated polymers by a simple addition reaction.

In order to understand the mechanism by which these disazo esters vulcanize rubber, Rabjohn[2] studied the reaction between ethyl azodicarboxylate and 2-methyl-2-butene. Although ethyl azodicarboxylate is a monofunctional derivative, its addition may be regarded as a model for the addition of disazodicarboxylates to the rubber molecule. In this case 2-methyl-2-butene must be regarded as a model of the isoprene unit in natural rubber.

It was shown by Rabjohn[2] that azodicarboxylates are added at the carbon atom which is in the α-position relative to the double bond.

$$C_2H_5O_2CN=NCO_2C_2H_5 + CH_3—C=CH—CH_3$$
$$CH_3$$

$$CH_2—C=CH—CH_3$$
$$CH_2$$
$$\longrightarrow \quad N—CO_2C_2H_5$$
$$NH—CO_2C_2H_5$$
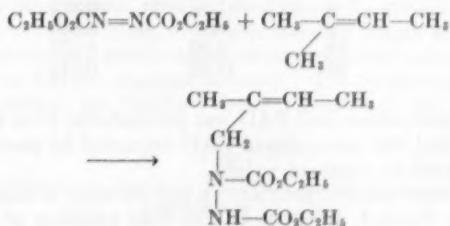
Consequently, disazodicarboxylates vulcanize rubber by forming crosslinks at the α-methylene carbon atoms between the polymer chains. According to Farmer[3], many compounds react with rubber in this position.

In the present investigation, ethyl azodicarboxylate and ethylene dis-ethyl azodicarboxylate were synthesized and some mechanical properties of the rubbers formed by their reaction with natural rubber were studied. The purpose

of the work was to study the influence of branching on the mechanical properties of natural rubber.

## EXPERIMENTAL

*Preparation of branched derivatives of natural rubber.*—To prepare branched derivatives of natural rubber, a definite amount of ethyl azodicarboxylate (EAD) in equivalent per cent relative to the basic molecular weight of the natural rubber was added to a definite amount (for example, 30 ml.) of 5% solution of smoked sheet (molecular weight $\sim$ 500,000) in benzene.

The reaction was conducted in a thermostat with stirring for two hours at 60°. Under these conditions, according to Flory, Rabjohn, and Shaffer[4], the ethyl azodicarboxylate adds quantitatively to natural rubber. The intrinsic viscosity of the solution was measured. The solutions were kept at room temperature in the dark to avoid degradative changes. The amount of reacted ethyl azodicarboxylate was determined by chemical analysis for nitrogen. The

TABLE I

EFFECT OF ETHYL AZODICARBOXYLATE ON THE VISCOSITY OF
BENZENE SOLUTIONS OF NATURAL RUBBER

| | Amount of EAD equivalent % | | Intrinsic viscosity | |
| | Added to rubber solution | Combined with rubber | | Literature data[4] |
| Solution | | | Measured | |
|---|---|---|---|---|
| Solution of rubber in benzene | 0 | — | 5.961 | 5.26 |
| Solution of rubber in benzene plus EAD after 2 hours at 60° C | 0 | — | 6.267 | 5.09 |
| | 1 | 0.90 | 5.73 | — |
| | 2 | 2.10 | 5.46 | 4.70 |
| | 3 | 2.89 | 5.80 | — |
| | 4 | 3.80 | 5.688 | 4.96 |
| | 5 | 4.35 | 3.367 | — |
| | 6 | 5.98 | 3.083 | — |
| | 7 | 6.81 | 1.695 | — |
| | 8 | 7.88 | 0.819 | 2.92 |
| | 9 | 8.70 | 0.728 | — |
| | 10 | 9.92 | 0.637 | — |
| | 20 | 19.80 | 0.343 | — |

derivative of natural rubber and EAD was precipitated from the benzene solution by ethyl alcohol, the uncombined EAD extracted by means of alcohol and the residue was dried to constant weight.

The effect of ethyl azodicarboxylate on the viscosity of natural rubber solutions is shown in Table I, where it is seen that addition of EAD to natural rubber decreases the viscosity as the amount of combined EAD increases.

*Preparation of crosslinked derivatives of natural rubber.*—Crosslinked films of natural rubber were prepared with the use of ethylene dis-ethyl azodicarboxylate (DEAD) as crosslinking agent.

The films were prepared by evaporation of the solvent at room temperature from a 5 per cent solution of natural rubber in benzene with additions of DEAD spread on a smooth glass surface and bounded by glass rings 10 cm. in diameter and 5 cm. high, which were hermetically ground to the glass surface. The vulcanization of the films was continued for 2 hours at 60°. After complete removal of the solvent under vacuum at room temperature, the mechanical

TABLE II

EFFECT OF DEAD ON THE MECHANICAL PROPERTIES OF FILMS

| Amount of DEAD in equiv. % | | | | Amount of DEAD in equiv. % | | | |
|---|---|---|---|---|---|---|---|
| Added to films | Found in films | Tensile strength in kg./cm² | Relative extension, % | Added to films | Found in films | Tensile strength in kg./cm² | Relative extension, % |
| 0.1 | 0.10 | 6.8 | 810 | 1.5 | 1.47 | 43.0 | 970 |
| 0.2 | 0.20 | 8.0 | 1220 | 2.0 | 1.99 | 79.0 | 1080 |
| 0.3 | 0.30 | 5.0 | 780 | 2.4 | 2.37 | 42.0 | 890 |
| 0.4 | 0.39 | 7.0 | 830 | 3.0 | 2.92 | 64.0 | 850 |
| 0.5 | 0.50 | 16.0 | 930 | 3.5 | 3.69 | 45.0 | 810 |
| 0.6 | 0.53 | 48.0 | 1150 | 4.0 | 4.00 | 114.0 | 1070 |
| 0.7 | 0.68 | 49.0 | 1180 | 5.0 | 4.92 | 52.0 | 680 |
| 0.8 | 0.79 | 58.0 | 1130 | 6.0 | 5.81 | 44.0 | 1120 |
| 0.9 | 0.87 | 37.0 | 1090 | 7.1 | 7.59 | 25.0 | 360 |
| 1.0 | 1.02 | 51.0 | 930 | | | | |

properties of the films were investigated. The amount of DEAD combined in the films was determined by analysis of the films for nitrogen. Before the analyses the films were extracted with ethyl alcohol to remove unreacted DEAD.

The effect of the amount of crosslinking agent DEAD on the mechanical properties is shown in Table II.

Another series of films was prepared from a solution of natural rubber to which 10 per cent (on the g-equiv. content) of ethyl azodicarboxylate (EAD) had previously been added. After two hours in a thermostat at 60° for completion of the reaction with EAD, various amounts of DEAD were added to the same solutions for vulcanization. The mechanical properties of the films so obtained were also tested. The results are shown in Table III.

The solubility of the films crosslinked with DEAD was tested in benzene. A 2 per cent sample was shaken in benzene for several days. All the films were insoluble in benzene, which showed that they were, in fact, crosslinked polymers.

*Extensibility and tensile strength diagrams.*—Dumbbell shaped specimens were cut from the rubber films, of 25 mm working length and 2 mm wide, and tested on the laboratory tensile tester at an extension rate of 0.08 cm./second (corresponding to 150 per cent per minute). The initial region of the diagram was used to evaluate the "static" elastic modulus of the rubber. The final

TABLE III

EFFECT OF (EAD + DEAD) ON THE MECHANICAL
PROPERTIES OF FILMS

| Amount added, as % of g-equiv. | | Total (EAD +DEAD) combined % | Tensile strength in kg./cm² | Relative extension, % |
|---|---|---|---|---|
| EAD | DEAD | | | |
| 10 | 0.1 | — | — | — |
| 10 | 1.0 | 10.8 | 10 | 1400 |
| 10 | 2.0 | 11.5 | 21 | 880 |
| 10 | 3.0 | 12.9 | 28 | 1050 |
| 10 | 4.0 | 14.0 | 33 | 860 |
| 10 | 5.0 | 15.2 | 21 | 590 |
| 10 | 7.0 | 16.7 | 20 | 510 |
| 10 | 10.0 | 19.8 | 17 | 340 |

point gave the tensile strength ($f$ is the force relative to the original cross section) and the relative extension at break as a percentage.   For all the specimens tested, both the extension diagrams and the tensile data determined from them varied greatly between different specimens cut from the same film.   The elastic modulus, found from the intial region of the extension diagram, was of the order $E_e \sim$ 4–10 kg./cm$^2$.

Table II contains average values for the tensile strength and extensibility of rubbers containing DEAD only.  A low content (up to 1 per cent) of the vulcanizing agent has little effect on the extension diagram.  As the DEAD content increases, the rubber becomes more rigid and strong.  The strength then decreases.  Rubbers containing 4 per cent DEAD had the highest strength.

Addition of 10 per cent EAD together with DEAD to the rubber resulted in an appreciable change in the properties of the rubber.  The films differed from films containing DEAD only, even in external appearance.  They were more tacky, were more difficult to remove from the glass on which they were cast, and were more like raw rubber than vulcanizates to the touch.  The tensile properties of these rubbers are shown in Table III; their strength was low, and the maximum tensile strength of specimens with 4 per cent DEAD was 33 kg./cm$^2$.

The manner in which the strength varied with the percentage content of DEAD remained the same as in films without EAD (see Table II).

Figure 1 shows load-extension diagrams for rubber containing 1 per cent DEAD (Curve $1$), and for rubber containing, in addition, 10 per cent EAD (Curve $2$).  The graphs show that these two rubbers differ greatly.  The rubber containing 10 per cent EAD showed very great extension up to $\epsilon_r \approx$ 1400 per cent at low loads (the span of the tensile tester was not sufficient to extend the specimens to break).  The rubber with DEAD only had a steeper load-extension diagram and a lower extension at break ($\epsilon_r \approx$ 800–1000 per cent).

The strongest of the rubbers so obtained were compared with rubber vulcanized with sulfur.  Figure 2 shows load-extension diagrams for the three
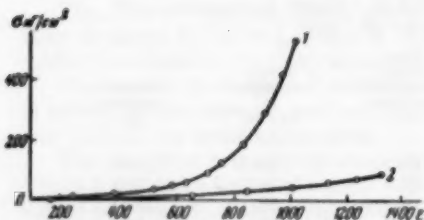


Fig. 1.—Variation of relative extension with load in rubber with 1 per cent DEAD: $1$, without addition; $2$, with 10 per cent EAD.
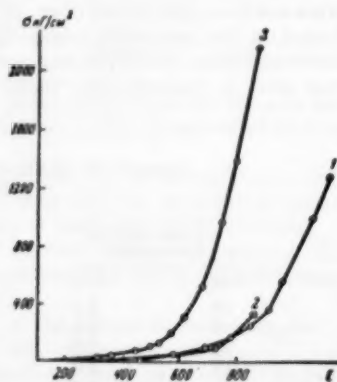
Fig. 2.—Variation of relative extension with load; $1$, rubber with 4 per cent DEAD; $2$, rubber with 4 per cent DEAD and 10 per cent EAD; $3$, rubber vulcanized with sulfur.

types of rubber; comparison of Curves *1* and *2* in Figure 2 shows that the properties of the rubber deteriorated on addition of 10 per cent EAD; the specimens broke at much lower extensions and correspondingly lower stresses. In addition, these rubbers both differ greatly in their mechanical properties from rubber vulcanized with sulfur (Curve *3*). Their strength was much lower than that of rubber vulcanized with sulfur; their load-extension diagrams do not show the characteristic steep rise of stress at the end of the extension; their extensibility is higher.

*Dynamic elastic modulus and mechanical losses.*—In addition to the load-extension diagrams, the dynamic elastic modulus and mechanical losses were determined for many specimens, both without EAD and containing 10 per cent EAD. The measurements were made by means of an apparatus described elsewhere[5].

A mechanical system, in which the test specimen served as the elastic element, was subjected to damped vibrations in the instrument.

The elastic modulus $E_g$ was determined from the formula

$$E_g = 4\pi^2 \frac{l_0}{S_0}\left(\frac{1}{T^2} - \frac{1}{T_c^2}\right) M_{\text{red}}.$$

Here $l_0$ and $S_0$ are the initial length and cross-section of the specimen; $T$ is the oscillation period of the mechanical system with the specimen; $T_c$ is the intrinsic oscillation period of the system (without the specimen); $M_{\text{red.}}$ is the reduced mass of the vibrating system.

The logarithmic decrement of the damping of the rubber, directly related to the tangent of the mechanical loss angle, was calculated from the formula

$$x = \pi \tan \delta = x_s - x_0$$

where $K_s$ and $K_0$ are the logarithmic damping decrements of the system with and without the specimen.

It must be pointed out that the frequencies used were low, in the range from 0.1 to 1 cycle/second. Because of this, it was not possible to determine the
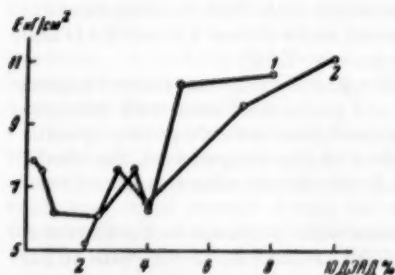


FIG. 3.—Variation of dynamic elastic modulus with percentage DEAD content; *1*, without EAD; *2*, with 10 per cent EAD.
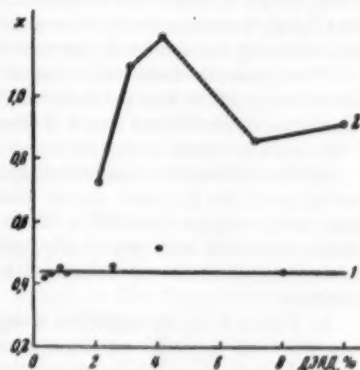
FIG. 4.—Variation of the logarithmic damping decrement with percentage DEAD content; *1*, without EAD; *2*, with 10 per cent EAD.
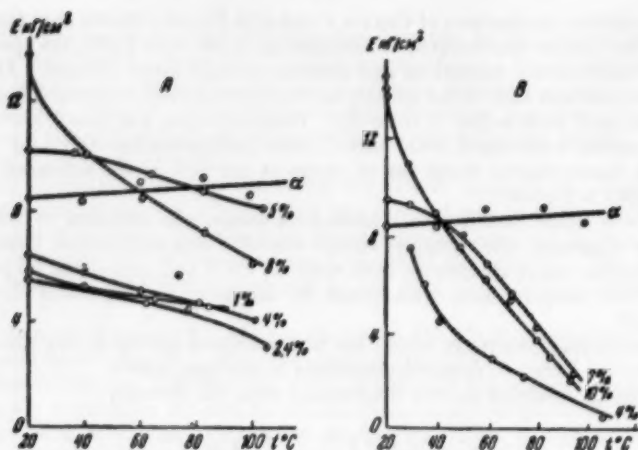
Fig. 5.—Variation of dynamic elastic modulus with temperature: A, rubbers without EAD;
B, rubbers with 10 per cent EAD; α, sulfur vulcanizate.

influence of frequency on the dynamic elastic modulus $E_g$ and the logarithmic damping decrement $K$.

The variation of $E_g$ and $K$ with percentage composition of DEAD in both types of rubber was studied at room temperature. The effect of temperature on these values was also studied for some rubbers. As the percentage content of DEAD increased in both types of rubber, the elastic modulus $E_g$ increased appreciably; this relationship is shown in Figure 3.

Figures 1, 2, and 3 show that addition of 10 per cent EAD had no significant effect on the dynamic elastic modulus. The absolute values of the dynamic modulus were higher than those of the static, but the nature of variation with DEAD content was the same.

At room temperature the mechanical losses of the rubbers were practically independent of the DEAD content (Figure 4, Curve 1). Addition of 10 per cent EAD, however, resulted in a sharp increase (about double) of the logarithmic damping decrement $K$ and correspondingly of tan δ (Figure 4, Curve 2).

The dynamic elastic modulus of the control (sulfur-vulcanized rubber) at room temperature was the same as that of rubber with DEAD. The logarithmic damping coefficient was 4–5 times as small as for rubber without EAD and 9–10 times as small as for rubber with 10 per cent EAD.

All the rubbers vulcanized with DEAD, without exception, showed a great variation of the dynamic elastic modulus and mechanical losses with temperature in the region 20–100°. While in sulfur-vulcanized rubber the dynamic elastic modulus was practically independent of the temperature, the elastic modulus of rubbers vulcanized with DEAD fell sharply with increase of temperature.

In Figure 5 the straight line α represents a sulfur vulcanizate, the Curves A represent rubbers with various amounts of DEAD, and B, rubbers with 10 per cent EAD.

Figure 6 shows the effect of temperature on mechanical loss. The Curve α represents a sulfur vulcanizate, and the others, rubbers with different contents of DEAD.
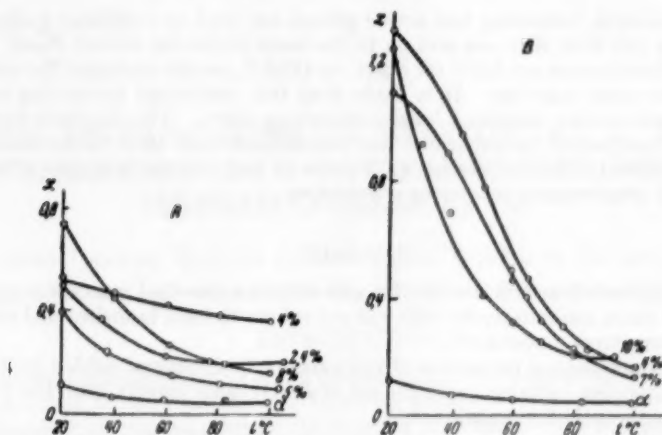
Fig. 6.—Variation of logarithmic damping decrement with temperature: A, rubbers without EAD; B, rubbers with 10 per cent EAD; a, sulfur vulcanisate.

Figures 5 and 6 show that the mechanical losses of the sulfur vulcanizate are slight and are influenced little by change of temperature. In rubbers with 10 per cent EAD the logarithmic damping decrement is large, and varies by a factor of 5–7 over the same temperature range.

## DISCUSSION

Flory, Rabjohn, and Shaffer[4] studied the extensibility diagrams and benzene swelling of vulcanizates made from natural rubber. The crosslinking agent used was DDAD (decamethylene-dis-n-decyl azodicarboxylate) which is a substance analogous to the DEAD used in our work.

They also used EAD to produce branching of the polymer chain. They concluded that the mechanical behavior of the vulcanizates so obtained did not greatly differ from that of sulfur vulcanizates; it is in agreement with the network theory and essentially reflects the increased volume concentration of crosslinks. They found that the properties of vulcanizates are little affected by the presence of branches in the rubber chains. The mechanical properties of the vulcanizates studied by us are very unlike those of sulfur vulcanizates of natural rubber. The differences are particularly great for the EAD-modified products. A striking fact is that the maximum strength was found in vulcanizates with 4 per cent DEAD, while Flory found a maximum for vulcanizates with 1 per cent DDAD.

In comparing our data with Flory's results[4] it is necessary to remember the different methods used for making the films. Flory and his coworkers cast their films in a ventilated cabinet at 60° for 2 hours. In our conditions vulcanization could proceed during the whole period of film formation at room temperature, and was completed during 2 hours at 60°.

The ethyl azodicarboxylate (EAD) side chains were introduced by Flory only after the films had been vulcanized by means of DDAD, that is, into crosslinked films. In our experiments EAD was first added to the natural rubber solution, the solution was then held for 2 hours at 60°, and only then was the crosslinking agent DEAD, added.

If molecules containing two active groups are used as crosslinking agents, there is a risk that they can add on to the same molecular rubber chain. In DDAD these groups are fairly far apart: in DEAD, on the contrary, the active groups are close together. It is likely that this compound forms ring compounds with rubber, and has a lower crosslinking effect. This accounts for the peculiar mechanical properties of the vulcanizates and their variation with DEAD content, which represents an increase of ring structures against a background of progressively increasing crosslinking.

## SUMMARY

1. Ethyl azodicarboxylate (EAD) and ethylene dis-ethyl azodicarboxylate (DEAD) react quantitatively with natural rubber to form branched and crosslinked derivatives, respectively.

2. The mechanical properties of vulcanizates from natural rubber containing side branches (obtained with the aid of EAD) differ greatly from the properties of unbranched vulcanizates.

3. Analysis of the load-extension diagrams shows that the introduction of EAD side chains into natural rubber results in the formation of vulcanizates with high extensions at low loads. Vulcanizates without EAD have steeper load-extension diagrams and lower extensions at break.

4. As the temperature rises from 20 to 100°, the elastic modulus and mechanical losses (or the logarithmic damping decrement) of vulcanizates crosslinked with DEAD decreases greatly (about 4–7 times). Addition of 10 per cent (g-equiv.) of EAD side chains approximately doubles the mechanical losses in comparison with vulcanizates without EAD.

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# THE VULCANIZATION OF ELASTOMERS. X. THE VULCANIZATION OF NATURAL RUBBER WITH THIURAM DISULFIDES (V) *

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## INTRODUCTION

Our studies on the kinetics of the thiuram disulfide vulcanization[1] has shown, among other things, that the two following processes have to be considered: the decrease of concentration of the thiuram disulfide and the increase of the amount of zinc dithiocarbamate as they relate to the vulcanization time. Both phenomena are for the largest part first order reactions. The decrease of the concentration of the thiuram disulfide proceeds faster than the increase of the zinc dithiocarbamate content of the vulcanizates.

We have already mentioned in previous publications of this series that kinetic relationships suggest the probable formation of an intermediate compound which upon further reaction leads to crosslinking under simultaneous formation of zinc dithiocarbamate. Therefore it should be expected that the crosslink creation process and the formation of the dithiocarbamate have the same rate, i.e., the dithiocarbamate formation and crosslinking process should be identical.

The change of the swelling of the vulcanizates with the vulcanization time is unquestionably a measure of the progress of crosslink formation. Therefore the problem arose of investigating the kinetics of the change of swelling of rubber during vulcanization with thiuram disulfide in order to decide whether the formation of the dithiocarbamate is actually related to crosslinking.

## EXPERIMENTAL

The experiments which are described in this article were performed with tetramethyl and tetraethylthiuram disulfide as curing agents. The vulcanizates were always prepared from pale crepe which was extracted exhaustively with acetone. One hundred grams of the mixture (compounded stock) contained 2.96 g. of tetraethyl or 2.4 g. of tetramethylthiuram disulfide and 5 g. of zinc oxide (active).

Since we have frequently described the preparation of thiuram disulfide vulcanizates, their extraction and the quantitative analysis of the extracts, a repetition of these procedures will be omitted. However, we will report briefly on the determination of swelling.

Samples of vulcanizates of any amount were allowed to stand with the solvent in closed weighing dishes for 48 hours in a 25° C thermostat. After this period of time the vulcanizates had reached their maximum swelling. The samples were quickly dried on hard filter paper and transferred to fresh weighing dishes which were carefully closed and weighed accurately. The swollen

samples then were dried in an oven for 16 hours (constant weight) at 80° C and weighed again. The weight difference is equal to the amount of absorbed solvent in grams. When this is divided by the weight of the dried sample, the amount, $Q_t$, of absorbed solvent per gram of vulcanizate is obtained.

We have proved experimentally that errors which are caused by the extraction of small amounts of material of low molecular weight such as thiuram disulfide and zinc dithiocarbamate are without significance, i e., the values for $Q_t$ are changed only very slightly if the dry weight before swelling is substituted for the dry weight after swelling. Therefore we omitted the application of such corrections.

It is obvious that the swelling maxima of vulcanizates of long reaction times which necessarily have a higher degree of crosslinking have to be determined

## TABLE I

### THIURAM DECREASE, DITHIOCARBAMATE INCREASE AND INVERSE SWELLING IN VARIOUS SOLVENTS DURING VULCANIZATION OF NATURAL RUBBER WITH TETRAETHYLTHIURAM DISULFIDE

| Vulcanization temp. (° C) | Vulcanization time (min.) | Thiuram disulfide (mole %) | Zinc dithiocarbamate (mole %) | $1/Q_t$ benzene | $1/Q_t$ cyclohexane | $1/Q_t$ isoamyl acetate |
|---|---|---|---|---|---|---|
| 100 | 180 | 30.8 | 18.5 | — | — | — |
| | 360 | 10.9 | 29.9 | 0.056 | 0.074 | — |
| | 540 | 6.2 | 39.9 | 0.091 | 0.116 | — |
| | 810 | 4.8 | 48.2 | 0.119 | 0.156 | — |
| | 1080 | 3.7 | 49.7 | 0.155 | 0.179 | — |
| | 1440 | — | 52.6 | 0.170 | 0.188 | — |
| | 1800 | — | 55.4 | 0.182 | 0.199 | — |
| | 2600 | — | 57.2 | 0.191 | 0.211 | — |
| | ∞ | — | — | 0.200 | 0.230 | — |
| 110 | 70 | 49.1 | 18.2 | — | — | — |
| | 140 | 26.7 | 28.2 | 0.056 | 0.079 | — |
| | 210 | 8.0 | 38.4 | 0.080 | 0.103 | — |
| | 300 | 3.0 | 43.8 | 0.115 | 0.135 | — |
| | 400 | — | 46.4 | 0.148 | 0.172 | — |
| | 600 | — | 51.5 | 0.173 | 0.193 | — |
| | 875 | — | 55.8 | 0.191 | 0.204 | — |
| | 1400 | — | 61.0 | 0.199 | 0.214 | — |
| | ∞ | — | — | 0.210 | 0.245 | — |
| 120 | 30 | 44.8 | 16.6 | — | — | — |
| | 60 | 17.0 | 26.9 | 0.054 | — | — |
| | 100 | 8.2 | 38.1 | 0.079 | — | — |
| | 150 | — | 46.3 | 0.135 | — | — |
| | 200 | — | 51.3 | 0.155 | — | — |
| | 300 | — | 55.0 | 0.162 | — | — |
| | 400 | — | 57.5 | 0.183 | — | — |
| | 600 | — | 61.0 | 0.193 | — | — |
| | ∞ | — | — | 0.200 | — | — |
| 130 | 15 | 43.9 | 17.1 | — | — | — |
| | 30 | 20.0 | 28.3 | 0.050 | 0.040 | 0.103 |
| | 45 | 6.0 | 37.8 | 0.075 | 0.097 | 0.158 |
| | 60 | 2.2 | 43.0 | 0.110 | 0.131 | 0.221 |
| | 80 | — | 47.2 | 0.121 | 0.155 | 0.260 |
| | 100 | — | 48.6 | 0.145 | 0.159 | 0.274 |
| | 150 | — | 54.5 | 0.148 | 0.181 | 0.293 |
| | 240 | — | 60.2 | 0.165 | 0.185 | 0.299 |
| | ∞ | — | — | 0.180 | 0.220 | 0.360 |

more accurately than those of only slightly crosslinked vulcanizates of short reaction times. If the crosslinking is only slight, the swelling is large and the gels have poor form stability which makes an accurate weight determination very difficult. The swelling maxima of weakly crosslinked vulcanizates are therefore accompanied by certain errors, whose magnitude will always remain uncertain. However, the analysis of the kinetics of swelling is not affected by this error as we will see later.

The value of the reciprocal of the amount of solvent absorbed, $1/Q$, per gram of vulcanizate under maximum swelling is especially suited for measuring the degree of crosslinking or vulcanization. This value is larger the smaller the swelling. For each case we determined the limiting value of crosslinking by plotting $\log 1/Q_t$ versus inverse time of vulcanization and by extrapolation of the resulting curve to $1/t = 0$. By this procedure the limiting values of crosslinking are obtained and are expressed by the reciprocal of maximum swelling, $1/Q_\infty$. We will omit the representation of graphical solutions for the end values of crosslinking because they offer nothing of special interest. However, we would like to mention that the values of $1/Q_\infty$ are subjected to variations due to the limited uniformity of the degree of degradation of the masticates. Thiuram disulfides should always produce the same number of crosslinks, provided that identical amounts of thiuram disulfides are applied, because they react practically independent of the temperature to give $\frac{2}{3}$ equivalents of zinc dithiocarbamate per mole of disulfide. The swelling maxima still may be different however, if the average molecular weights of the masticates on which the vulcanizates are based are not identical. Identical values for $1/Q_t$ at constant concentrations of thiuram disulfides may be expected for those cases where the masticates are identical. However, this may only be observed experimentally as long as no reversion occurs.

## TABLE II

DITHIOCARBAMATE INCREASE AND INVERSE SWELLING IN VARIOUS
SOLVENTS DURING VULCANIZATION OF NATURAL RUBBER WITH
TETRAMETHYLTHIURAM DISULFIDE

| Vulcanization temp. ($^\circ$C) | Vulcanization time (min.) | Zinc dithiocarbamate (mole %) | $1/Q_t$ benzene | $1/Q_t$ cyclohexane | $1/Q_t$ isoamyl acetate |
|---|---|---|---|---|---|
| .110 | 90 | 24.1 | 0.048 | — | 0.096 |
| | 130 | 36.2 | 0.058 | 0.075 | 0.104 |
| | 170 | 41.8 | 0.090 | 0.099 | 0.181 |
| | 230 | 48.3 | 0.121 | 0.136 | 0.224 |
| | 290 | 52.1 | 0.138 | 0.156 | 0.264 |
| | 410 | 58.7 | 0.166 | 0.187 | 0.294 |
| | 530 | 63.8 | 0.172 | 0.191 | 0.317 |
| | 850 | 64.0 | 0.188 | 0.209 | 0.341 |
| | ∞ | — | 0.200 | 0.225 | 0.366 |
| 120 | 40 | 23.1 | 0.041 | | 0.104 |
| | 60 | 38.0 | 0.078 | | 0.131 |
| | 80 | 45.6 | 0.113 | | 0.204 |
| | 110 | 50.7 | 0.134 | | 0.252 |
| | 140 | 54.9 | 0.150 | | 0.285 |
| | 200 | 58.8 | 0.166 | | 0.311 |
| | 260 | 62.4 | 0.175 | | 0.328 |
| | 350 | 66.4 | 0.184 | | 0.341 |
| | ∞ | — | 0.495 | | 0.365 |

## RESULTS AND DISCUSSION

As we have already mentioned, the swelling maxima which are discussed in this paper were obtained from vulcanizates which were prepared with tetramethyl and tetraethylthiuram disulfide. Both compounds gave the same results. Therefore, we limit the presentation to the complete reproduction of
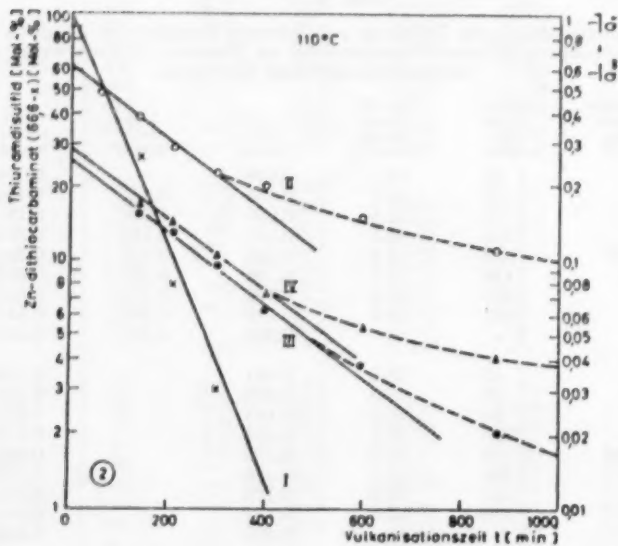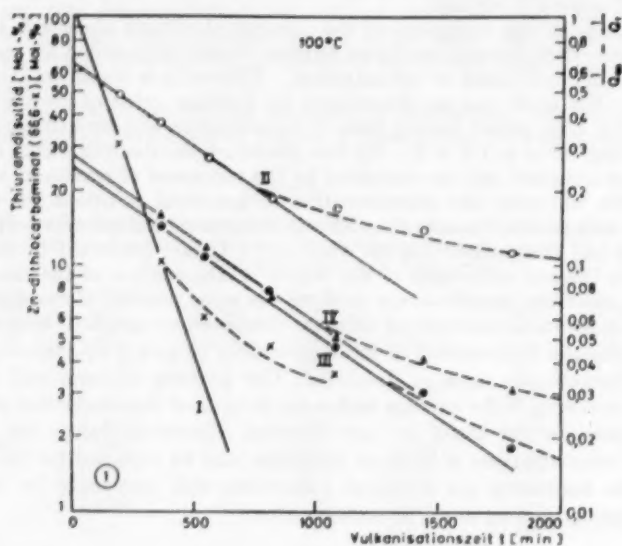
results as obtained from vulcanizates of natural rubber and tetraethylthiuram disulfide, and we will supplement these results with two experimental series with tetramethylthiuram disulfide as a vulcanizing agent.
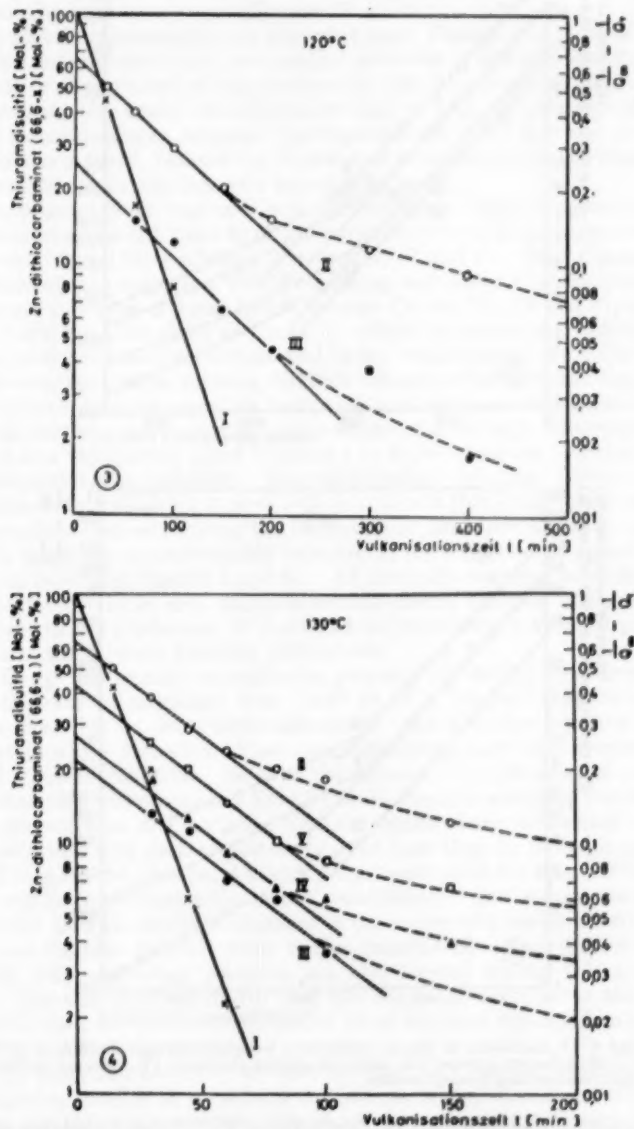


Figs. 1–4.—Vulcanization of natural rubber with tetraethylthiuram disulfide at 100°, 110°, 120° and 130° C. I, thiuram decrease; II, dithiocarbamate increase; III, reciprocal swelling (benzene); IV, reciprocal swelling (cyclohexane); V, reciprocal swelling (isoamyl acetate).
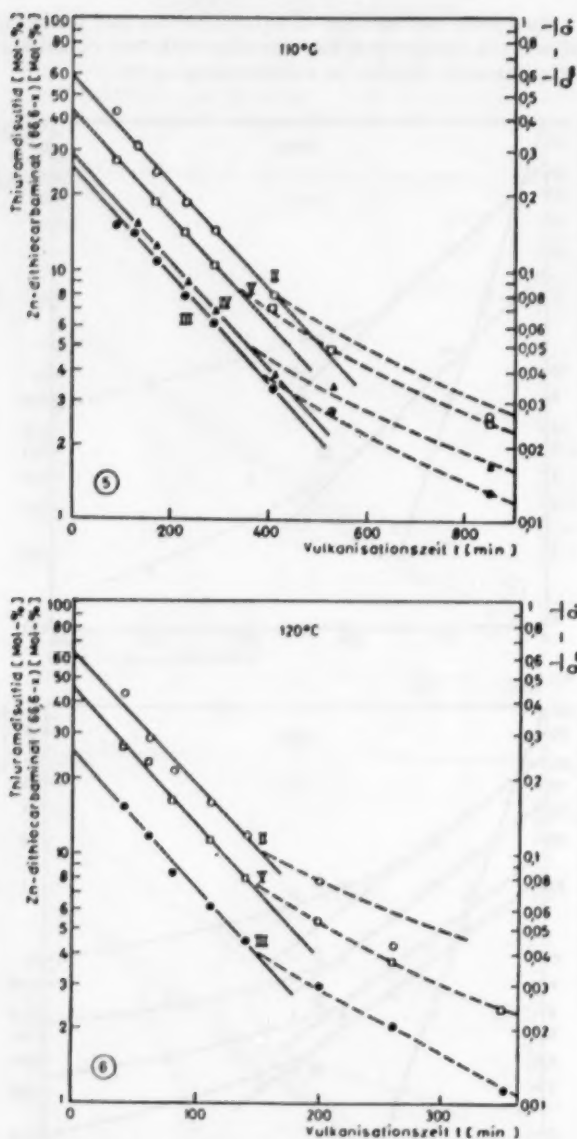
FIGS. 5 and 6.—Vulcanization of natural rubber with tetramethylthiuram disulfide at 110° and at 120° C. II, dithiocarbamate increase; III, reciprocal swelling (benzene); IV, reciprocal swelling (cyclohexane); V, reciprocal swelling (isoamyl acetate).

The results are summarized in Tables I and II. Table I contains: the decrease of concentration of thiuram disulfide (Column 3), the increase of the zinc dithiocarbamate content of the vulcanizates in mole per cent of the applied

thiuram disulfide (Column 4), as well as the crosslinking, measured by means of the reciprocal swelling, $1/Q_t$ in benzene (Column 5), cyclohexane (Column 6) and isoamyl acetate (Column 7). The experiments of Table I were performed at 130°, 120°, 110° and 100° C. For each case the vulcanization times were varied over a wide range (Column 2).

The kinetic relationships are apparent from Figures 1 to 6. On the left ordinates (logarithmic scale) the residual amounts of thiuram disulfide (mole per cent) or the amount of dithiocarbamate $(66.6 - x)$ are plotted. On the right ordinate (log scale) the differences $1/Q_\infty - 1/Q_t$ are plotted. Abscissa: time of vulcanization in minutes. In Figures 5 and 6 the decrease of thiuram disulfide was omitted, because the figures deal with control measurements with tetramethylthiuram disulfide as a vulcanizing agent.

Now it becomes obvious as to how the increase in crosslinking, expressed by $1/Q_t$, follows a first order law at all temperatures over a wide range of reaction. This is valid for all three solvents (Curves III, IV and V). Now it is also clear, as we have always suspected, that crosslinking and increase in dithiocarbamate content are processes of equal speed, because Curves III, IV and V practically always have the same slope as Curve II, which represents the kinetics of the increase of the dithiocarbamate content in the vulcanizates. It is also obvious that the decrease of the thiuram disulfide concentration proceeds significantly faster (Curve I) than crosslink formation and increase of dithiocarbamate. Although this was shown only by means of experiments with tetraethylthiuram disulfide as a vulcanizing agent (Figures 1 to 4) the same can be expected with tetramethylthiuram disulfide. The relationship between dithiocarbamate formation and crosslinking is obviously so intimate that even deviations which we have often observed during the formation of dithiocarbamate in the slight reaction range are unquestionably repeated in the course of reciprocal swelling (compare especially Figures 5 and 6). All these observations seem to indicate that the formation of zinc dithiocarbamate during thiuram vulcanization is equivalent to the production of crosslinks and therefore is also a result of the reaction of the thiuram disulfide with rubber.

D. Craig[2] has recently submitted a proposal correlating his interpretation of the thiuram vulcanization with "our" 66 mole per cent transformation of thiuram disulfide to zinc dithiocarbamate. He also developed a reaction mechanism which furnishes 66 per cent dithiocarbamate with respect to the applied thiuram disulfide. He is of the opinion that the creation of dithiocarbamate does not necessarily have to be the result of a crosslinking reaction[3]. At the present time it is our belief that the results of our investigations do not agree very well with such an assumption, at least they do not support it.

D. Craig has the view point that in a final analysis of the thiuram vulcanization it will be found that sulfur causes crosslinking. At the same time he is of the opinion that the sulfur is liberated in the course of a reaction between zinc oxide and thiuram disulfide prior to the crosslinking. Zinc dithiocarbamate together with still other products are also formed during this time. We believe that this should indicate that the Maximoff reaction[4] is the decisive step in the thiuram vulcanization but as far as we know this reaction has never been quantitatively investigated.

In the meantime however, we have accepted D. Craig's concept (of thiuram vulcanization) insofar as it pertains to the crosslinking of poly-1,5-dienes with thiuram disulfides across sulfur bridges which we now consider a probable reaction. We have recently disclosed a reaction mechanism (and opened it for discussion) which makes allowances for the formation of sulfur bridges[5].

However, we have not made the assumption that the sulfur is created in a preceding reaction which is not directly connected with crosslinking. If, on the other hand, the Maximoff reaction is hidden behind the things which we have discovered about the thiuram vulcanization, then we have to ask ourselves why, e.g., the rate of the thiuram disulfide decrease among the various 1,5-dienes is so different and why in all the cases which we have investigated the dithiocarbamate formation proceeds slower than the thiuram decrease. Furthermore, the different quotients, $k_D/k_{Dt}$, would not be easy to explain and finally, the rate equivalence of reciprocal swelling and dithiocarbamate formation do not command a conclusion which would see no relation between crosslinking and dithiocarbamate formation. But in order to decide for either one of the theories, many more investigations are required.

We intend to investigate intensively the Maximoff reaction and therefore are continuing our work in this field.

## SUMMARY

The kinetics of crosslinking natural rubber during vulcanization with tetramethyl and tetraethylthiuram disulfide was investigated. The following results were derived:

1. The increase of crosslinking during vulcanization which was measured by the change of reciprocal swelling is first order over a wide range of reaction time and temperature.

2. During vulcanization, crosslinking and dithiocarbamate formation are reactions which proceed with identical rate. From this we had to conclude that the formation of dithiocarbamate is the immediate cause of the crosslink formation.

3. The concentration of the thiuram disulfide decreases much faster with respect to vulcanization time than crosslinking increases. In other words, the thiuram decrease can only be considered a reaction which precedes crosslinking.

## ACKNOWLEDGMENTS

## REFERENCES

[1] Scheele, Lorenz and Dummer, *Kautschuk u. Gummi* 7, WT 273 (1954); 8, WT 2 and 27 (1955); Scheele and Lorenz, *Kautschuk u. Gummi* 8, WT 85 (1955); Scheele and Bielstein, *Kautschuk u. Gummi* 8, WT 251 (1955); Scheele and Stange, *Kautschuk u. Gummi* 9, WT 110 (1956); Scheele and Toussaint, *Kautschuk u. Gummi* 9, 149 (1956); 9, 243–7 (1956); compare also: Scheele, *Kolloid-Z* 146, 14 (1956), as well as Scheele et al. RUBBER CHEM. & TECHNOL. 29, 1 (1956).

[2] Craig, *J. Polymer Sci.* 20, 197 (1956).

[3] D. Craig believes he has to arrive at this conclusion because we have not talked about an induction period in connection with the dithiocarbamate formation, among other things, during vulcanization with thiuram monosulfide and sulfur (1 mole monosulfide per gram atom of sulfur). We will shortly show, however, that such an induction period was discovered by us during vulcanization of Perbunan with tetramethylthiuram monosulfide and sulfur. Therefore we ask ourselves whether the delayed dithiocarbamate formation during vulcanization of natural rubber with tetramethylthiuram monosulfide and sulfur, which at that time we called the heating-up period, was not actually an induction period.

[4] Maximoff, *Caoutchouc et guttapercha* 18, 944 and 986 (1921).

[5] Bielstein and Scheele, *Kolloid-Z.* 147, 152 (1956).

# THE VULCANIZATION OF ELASTOMERS. XI. THE VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF MERCAPTOBENZOTHIAZOLE. I *

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## INTRODUCTION

The technically important vulcanization of rubber[1] by means of sulfur is often accomplished with the addition of mercaptobenzothiazole as an accelerator. Numerous researches have been published dealing with this vulcanizing reaction and in many instances tests have been made in order to answer the questions regarding mechanism[2]. As is well known, there are two methods of procedure for explaining a chemical process. One is to isolate and identify the products of the reaction. The other endeavors to clarify the reaction mechanism through study of the kinetics.

Experience has shown that through transformations of macromolecular substances the isolation and identification of the reaction products are often rendered more difficult so that such examinations are undertaken more appropriately and with greater success by following the examples of model low molecular weight substances. On the other hand, kinetic studies are generally possible even for the transformations of macromolecular substances but the results convey data on the course of reaction rather than on the end product and its makeup. If we now ask what transpires from the studies of either kind in regard to the accelerated vulcanization of rubber, we conclude that the information presently obtainable is still quite incomplete. The major portion of the work published so far in this field deals mostly with physico-technical characteristics as criteria for the course of the reaction, while kinetics[3] or preparative work[4] is available only in individual cases. A renewed and systematic research of accelerated sulfur vulcanization is, therefore, a needed contribution. This paper gives a report on the kinetics of sulfur vulcanization accelerated with mercaptobenzothiazole.

## EXPERIMENTAL

*Preparation, extraction and analysis of vulcanizates.*—All vulcanizates were made from pale crepe which had been extracted with acetone for 48 hours. Inasmuch as we have previously reported on the preparation of vulcanizates[5], we shall refrain from going again into details. Our investigations will limit themselves, generally, to compounds which for every 100 grams of mixture contain 3.2 grams (0.1 gram atom) sulfur and 2.088 grams (12.5 millimoles) mercaptobenzothiazole or 2.48 grams (6.25 millimoles) zinc salt of mercaptobenzothiazole. This corresponds to a mole ratio of 1 mole $S_8$:1 mole mercaptobenzothiazole or, respectively, 2 moles $S_8$:1 mole zinc salt of mercaptobenzothiazole.

If the mixtures contained zinc oxide, the addition amounted to 4.07 grams (50.0 millimoles) for each 100 grams of mixture.

Free sulfur was extracted in darkness, at room temperature, with alcohol-benzol (1:2). For this purpose about 2 grams of the ground vulcanizate were repeatedly treated (generally 3 times) for two or three days, each time with 70–80 ml. of solvent. In the combined extracts we determined the elementary sulfur as thiocyanate after treatment with potassium cyanide. The exact procedure for this analysis through conductometric titration with silver nitrate was recently described by us in detail[6].

The extraction of mercaptobenzothiazole and of the zinc salt of mercapto-benzothiazole was done with chloroform at room temperature. In this instance the extraction was quantitative after four changes of the solvent during 2 or 3 days. After combining the extracts, a part of the solvent was distilled away and the remainder was made up to an accurately measured volume. The determination of mercaptobenzothiazole + zinc salt of mercaptobenzothiazole then followed. This was by titration with an alcoholic iodine solution as previously reported[6], the ratio of the two components not being determined.

*Quantitative determination of swelling.*—Square sheets of the vulcanizate (about 1 g. each) were submerged in benzene in a 25° C thermostat for 48 hours in a closed container, then quickly dried with hard filter paper and placed in a weighing tube which was carefully sealed and immediately weighed. The weight of the swollen gel is obtained by subtracting the weight of the empty container. The swollen vulcanizates were kept for 16 hours in a drier at 80° C and again weighed. The amount in grams of the absorbed solvent is obtained as the difference between the weight of the swollen gel and the dry weight after swelling. Dividing by the dry weight of the testpiece after swelling will give the weight, $Q_t$, of the absorbed solvent for each gram of vulcanizate. In calculating $Q_t$ we shall omit making any corrections to account for the solution of certain component parts of the vulcanizates[7] (such as sulfur, accelerator and low molecular weight rubber) since the values of $Q_t$ are thereby changed so little that the kinetic analysis is not affected.

*Preliminary tests.*—A test for the reaction of mercaptobenzothiazole with natural rubber was made as follows: 5000.0 mg. of mercaptobenzothiazole were mixed into 20.0 g. of natural rubber on a mill and the mixture heated in a closed mold for two hours at 140° C. After this, the product showed no elastic character and, in fact, it behaved like the original masticated material. After heating, 2 g. of this mixture were mixed with chloroform and lightly warmed. The clear solution which resulted was cooled, made up to 100 ml. and the mercaptobenzothiazole was iodometrically determined. In this way the amount found was 97.8 per cent of that started with. A similar experiment with a mixture containing 500.0 mg. of zinc salt of mercaptobenzothiazole in place of the mercaptobenzothiazole indicated that there was no reaction. We were able to recover the zinc salt in theoretical yield (100.5%).

The reaction of mercaptobenzothiazole with zinc oxide in bromobenzene was carried out as follows: 200 ml. bromobenzene and 1.0175 g. (12.5 millimoles) zinc oxide were heated to 108° C while stirring in a 3-necked flask equipped with a stirrer, reflux condenser and thermometer. Then 522.5 mg. (3.125 millimoles) mercaptobenzothiazole in 50 ml. bromobenzene were added. Specimens taken after various periods were quickly cooled, passed through a membrane filter, and the mercaptobenzothiazole content established (conductometric titration with silver nitrate) as well as the sum of mercaptobenzothiazole + zinc salt of mercaptobenzothiazole (iodometric titration[8]). We found here

that the mercaptobenzothiazole content, after one hour was 33.4 per cent and after three hours 13.9 per cent, while the sum of mercaptobenzothiazole + its zinc salt always showed up as 100 per cent.

### TABLE I

#### VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF MERCAPTOBENZOTHIAZOLE AND ZINC OXIDE

##### Composition of mixture

| | |
|---|---|
| Sulfur | 3.206 g. (0.1 gram atom) |
| Mercaptobenzothiazole | 2.088 g. (0.0125 mole) |
| Zinc oxide | 4.070 g. (0.05 mole) |
| Rubber | 90.636 g. |

| Cure temperature, C° | Cure time, minutes | Free S, % | Unreacted accelerator, % | $\frac{1}{Q_i}$ |
|---|---|---|---|---|
| 110 | 200 | 81.2 | — | — |
| | 400 | 70.4 | — | — |
| | 750 | 58.8 | — | — |
| | 1000 | 50.6 | — | — |
| | 1310 | 40.7 | — | — |
| | 1800 | 29.5 | — | — |
| | 3000 | 13.3 | — | — |
| | 4400 | 7.0 | — | — |
| 120 | 90 | 75.6 | 97.6 | 0.0524 |
| | 180 | 62.1 | 96.3 | 0.0597 |
| | 300 | 56.1 | 95.2 | 0.0673 |
| | 420 | 45.7 | 94.3 | 0.0914 |
| | 570 | 37.5 | 93.6 | 0.1055 |
| | 720 | 30.1 | 92.6 | 0.1225 |
| | 930 | 21.8 | 91.9 | 0.1303 |
| | 1260 | 13.5 | 90.0 | 0.1475 |
| | ∞ | | | 0.166 |
| 130 | 30 | 80.0 | — | — |
| | 60 | 71.2 | 98.6 | 0.0433 |
| | 90 | 63.0 | 96.2 | 0.0550 |
| | 120 | 54.3 | 95.7 | 0.0696 |
| | 180 | 42.1 | 94.4 | 0.0917 |
| | 240 | 30.1 | 91.5 | 0.1160 |
| | 360 | 15.9 | 89.8 | 0.1330 |
| | 540 | 7.5 | 86.4 | 0.1460 |
| | ∞ | | | 0.156 |
| 140 | 15 | 84.2 | 96.9 | 0.0461 |
| | 30 | 68.7 | 94.9 | 0.0827 |
| | 45 | 56.1 | 91.3 | 0.0881 |
| | 60 | 47.8 | 89.5 | 0.118 |
| | 90 | 30.2 | 89.0 | 0.137 |
| | 120 | 23.4 | 85.2 | 0.148 |
| | 180 | 11.1 | 81.7 | 0.165 |
| | 240 | 4.5 | 80.0 | 0.173 |
| | ∞ | | | 0.183 |
| 150 | 10 | 79.5 | 96.5 | 0.0598 |
| | 20 | 60.3 | 91.2 | 0.0893 |
| | 30 | 43.9 | 88.5 | 0.116 |
| | 40 | 33.5 | 82.4 | 0.139 |
| | 60 | 19.3 | 80.6 | 0.147 |
| | 80 | 12.5 | 77.6 | 0.159 |
| | 100 | 8.4 | 78.4 | 0.161 |
| | 120 | 4.7 | 76.9 | 0.170 |
| | ∞ | | | 0.175 |

## RESULTS AND DISCUSSION

*Vulcanization of natural rubber with sulfur in the presence of mercaptobenzo-thiazole or its zinc salt in the presence of zinc oxide.    The kinetics of sulfur com-bination.*—The reaction of natural rubber with sulfur accelerated with mercapto-benzothiazole, or its zinc salt, was studied in the temperature range of 110° to 150° C.    In Table I, Column 3 and in Table II, Column 3, we summarize the free sulfur found in the vulcanizates and expressed as percentage of the amount used in the recipe.    The kinetic evaluation of the results shows that over the

### TABLE II

VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF ZINC BENZOTHIAZOLYLMERCAPTIDE AND ZINC OXIDE

Composition of mixture

| | |
|---|---|
| Sulfur | 3.206 g. (0.1 gram atom) |
| Zinc benzothiazolylmercaptide | 2.48 g. (0.00625 mole) |
| Zinc oxide | 4.07 g. (0.05 mole) |
| Rubber | 90.244 g. |

| Cure temperature, C° | Cure time, minutes | Free S, % | Unreacted accelerator, % | $\frac{1}{Q_t}$ |
|---|---|---|---|---|
| 120 | 90 | 82.2 | 98.1 | — |
| | 180 | 66.2 | 97.1 | 0.0606 |
| | 300 | 57.9 | 95.6 | 0.0704 |
| | 420 | 46.9 | 94.1 | 0.0950 |
| | 600 | 35.2 | 93.5 | 0.124 |
| | 800 | 24.5 | 91.2 | 0.143 |
| | 1000 | 19.0 | 90.1 | 0.160 |
| | 1250 | 14.1 | 88.3 | 0.173 |
| | ∞ | | | 0.200 |
| 130 | 30 | 89.0 | — | |
| | 60 | 75.7 | 97.7 | 0.0474 |
| | 90 | 69.3 | 96.1 | 0.0550 |
| | 120 | 60.7 | 94.9 | 0.0714 |
| | 180 | 50.7 | 93.3 | 0.0855 |
| | 240 | 36.7 | 88.3 | 0.110 |
| | 360 | 23.0 | 85.3 | 0.140 |
| | 540 | 9.2 | 84.8 | 0.158 |
| | ∞ | | | 0.185 |
| 140 | 15 | 89.5 | 97.0 | — |
| | 30 | 79.2 | 95.0 | 0.0452 |
| | 45 | 65.6 | 91.5 | 0.0535 |
| | 60 | 57.6 | 89.6 | 0.075 |
| | 90 | 33.3 | 88.9 | 0.099 |
| | 120 | 23.2 | 85.3 | 0.114 |
| | 180 | 10.7 | 81.7 | 0.133 |
| | 240 | 5.0 | 81.0 | 0.143 |
| | ∞ | | | 0.153 |
| 150 | 10 | 83.5 | — | — |
| | 20 | 64.3 | 92.3 | 0.054 |
| | 30 | 54.4 | 89.3 | 0.086 |
| | 40 | 41.5 | 86.4 | 0.097 |
| | 60 | 20.3 | 85.1 | 0.118 |
| | 80 | 11.7 | 83.2 | 0.130 |
| | 100 | 6.5 | 81.2 | 0.122 |
| | 120 | 3.5 | 78.3 | 0.116 |
| | ∞ | | | 0.150 |
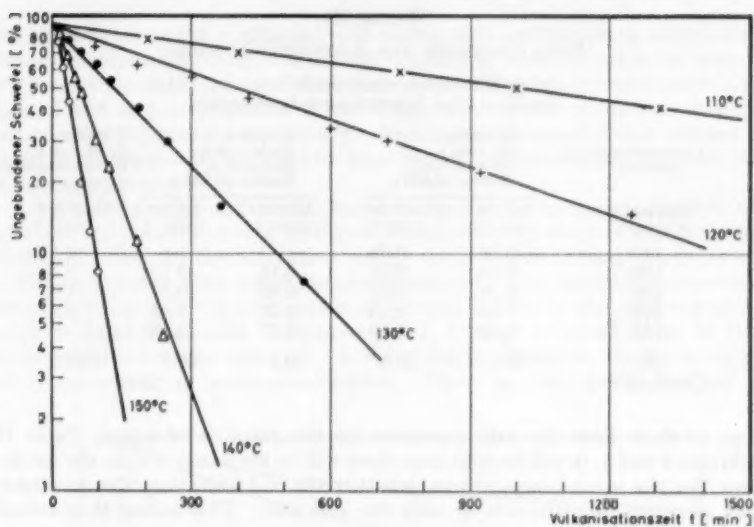
FIG. 1.—Decrease in sulfur concentration as a first order reaction for natural rubber vulcanizates accelerated with mercaptobenzothiazole in the presence of zinc oxide. The ordinate is free sulfur and the abscissa is cure time.

entire temperature range the sulfur diminishes according to the first order reaction law because if one plots the log of the free sulfur against the reaction time one obtains straight lines (Figures 1 and 2). If we establish from the
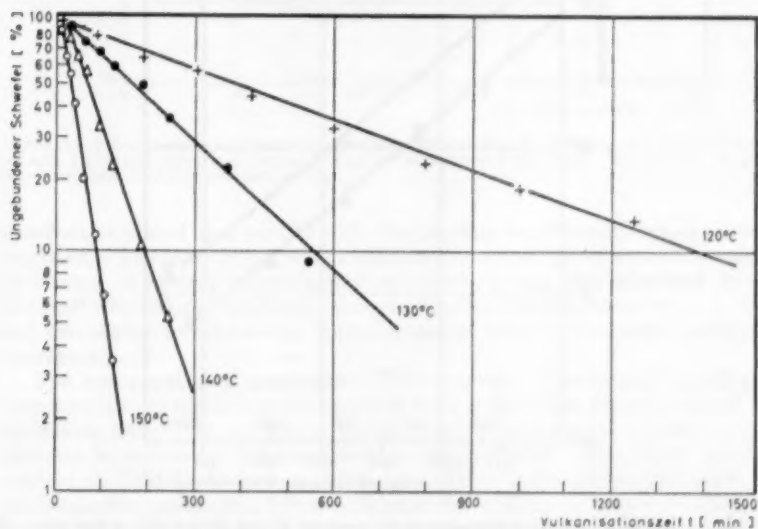


FIG. 2.—This is the same as Figure 1, except that the data are for acceleration with the zinc salt of mercaptobenzothiazole.

## TABLE III

### RATE CONSTANTS AND ACTIVATION ENERGIES

M = Mercaptobenzothiazole
Zn-M = Zinc Benzothiazolylmercaptide

| Composition of mixture | S 3.206 g. M 2.088 g. ZnO 4.070 g. Rubber 90.636 g. | | S 3.206 g. Zn-M 2.48 g. ZnO 4.07 g. Rubber 90.244 g. | | S 3.206 g. Zn-M 2.48 g. Rubber 94.314 g. |
|---|---|---|---|---|---|
| Temperature of cure, C° | $k_2{}^I \cdot 10^8$ (min.$^{-1}$) | $k_2{}^I \cdot 10^8$ (min.$^{-1}$) | $k_2{}^I \cdot 10^8$ (min.$^{-1}$) | $k_2{}^I \cdot 10^8$ (min.$^{-1}$) | $k_2{}^I \cdot 10^8$ (min.$^{-1}$) |
| 110 | 0.06 | 0.06 | — | — | 0.17 |
| 120 | 0.15 | 0.15 | 0.16 | 0.16 | 0.48 |
| 130 | 0.46 | 0.51 | 0.42 | 0.37 | 1.02 |
| 140 | 1.23 | 1.18 | 1.27 | 1.15 | 2.88 |
| 150 | 2.70 | 2.79 | 2.77 | 2.65 | — |
| $E_A$ [kcal./mole] | 30.5 | 30.5 | 30.5 | 30.5 | 29.5 |

slope of these lines the rate constants for the reaction of sulfur, Table III, Columns 2 and 4, it will be seen that these will be the same, within the limits of error, for the same temperatures, whether the vulcanization was accelerated with mercaptobenzothiazole or with the zinc salt. This means that actually
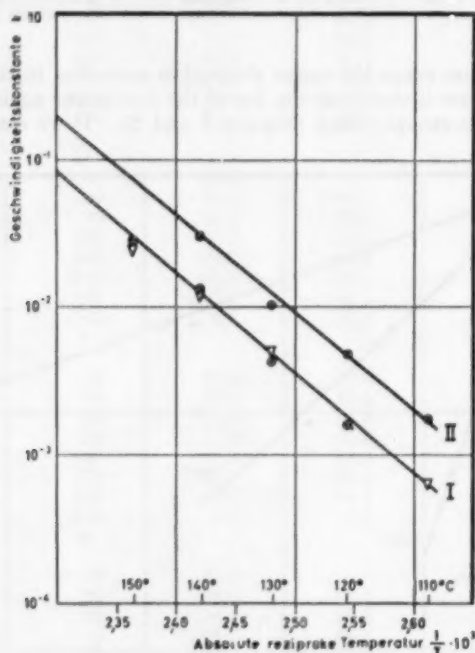


FIG. 3.—Arrhenius plots for vulcanization in the presence (I) and absence (II) of zinc oxide. The ordinate is first order velocity constant and the abscissa reciprocal of absolute temperature. Data for mercaptobenzothiazole acceleration are indicated by triangles and data for the zinc salt acceleration by circled crosses. See Table III for data.

the same acceleration is attained with mercaptobenzothiazole as with the zinc benzothiazolylmercaptide[9]. It is therefore easy to assume that in the presence of mercaptobenzothiazole and zinc oxide, zinc benzothiazolylmercaptide is first formed and as a consequence it would appear that this compound should be regarded as the actual accelerator[10]. Earlier in this paper it was pointed out that the zinc salt is formed rapidly from mercaptobenzothiazole and zinc oxide in bromobenzene.

If we plot the log of the rate constants against the reciprocal absolute temperature we obtain Curve $I$ in Figure 3 and from the slope of this we obtain 30.5 kcal./mole for the activation energy for reaction of natural rubber with sulfur accelerated with mercaptobenzothiazole or zinc benzothiazolylmercaptide, while for sulfur vulcanization of natural rubber in the presence of zinc oxide without accelerator D. Spence and J. Young[11] obtained 35 to 36 kcal./ mole as the activation energy[12]. A reduction in activation energy could well be characteristic of some accelerators. Their manner of effectiveness can
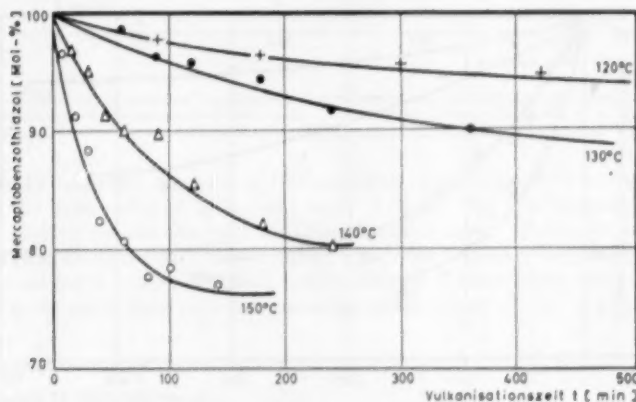


Fig. 4.—The decrease in accelerator concentration with cure time for sulfur-cured natural rubber vulcanizates accelerated with mercaptobenzothiazole in the presence of zinc oxide. The ordinate is accelerator concentration and the abscissa cure time.

therefore be placed on a parallel with that of other catalysts in organo-chemical reactions. The same result with respect to the reduction of activation energy by means of certain vulcanization accelerators was also observed by M. Gordon[13] who utilized kinetically the quantitative investigations by R. L. Zapp and co-workers[14] on the sulfur vulcanization of butyl rubber with various accelerators.

*The consumption of accelerator.*—The decrease of mercaptobenzothiazole concentration in relation to the reaction time is shown in Figure 4 where vulcanization time, $t$, in minutes is plotted against concentration remaining accelerator in per cent of the mercaptobenzothiazole used. The results are summarized in Table I, Column 4. Only the sum of mercaptobenzothiazole and zinc benzothiazolylmercaptide was determined without reference to the value of each individual component because from results thus far it can be concluded that in the presence of zinc oxide both compounds will give the same result. Figure 4 shows clearly that the decrease of accelerator concentration depends

on temperature. The higher the vulcanizing temperature selected, the more accelerator will be consumed. A reduction in the concentration of accelerator will take place only as long as free sulfur is contained in the mixture. When the sulfur in the mixture is consumed, however, the amount of accelerator in the vulcanizate will remain constant. This means, therefore, that the consumption of accelerator is tied to the combination of sulfur with rubber. This conclusion is also confirmed, indirectly, by the preliminary tests just described in which no reaction occurred when rubber was heated under vulcanizing conditions with mercaptobenzothiazole or its zinc salt. We also tested the possibility that the accelerator consumed during the reaction might be present as benzothiazolyl disulfide, but we could not detect this compound in any extracts from the vulcanizates. As we know, benzothiazolyl disulfide reacts with natural rubber, although slowly, with network formation and with the formation of mercaptobenzothiazole[15,16]. So we prefer to assume that the absence of dibenzothiazolyl disulfide in the vulcanizate extracts is not necessarily to be
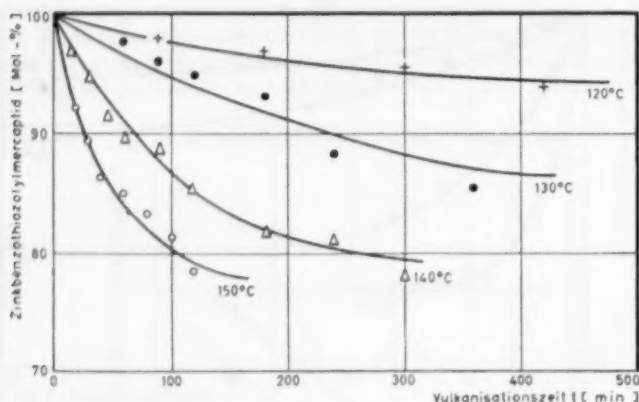


FIG. 5.—The decrease in accelerator concentration with time for sulfur-cured natural rubber vulcanizates accelerated with the zinc salt of mercaptobenzothiazole in the presence of zinc oxide. The ordinate is accelerator concentration and the abscissa cure time.

considered as a proof for the nonexistence of this compound in sulfur vulcanization accelerated by mercaptobenzothiazole. We could not determine, from the results of our analysis, in what order of reaction the consumption of the accelerator occurs, because the kinetic evaluation is rendered difficult by the relatively small consumption and the proportionately larger errors in analysis (1–2%) that may result. Figure 5 and Table II, Column 4, show that we find quantitatively the same relation in regard to decrease of accelerator, even in the case of vulcanization accelerated with the zinc salt of mercaptobenzothiazole.

With the help of swelling measurements we endeavored to obtain an insight into the reactions of network formation because, as well known, a vulcanizate will swell less, the more it is crosslinked. The reciprocal swelling, $1/Q_t$, therefore could be regarded as a measure of crosslinking. As already explained, by $Q_t$ we mean the quantity of solvent (benzene) in grams, which one gram of vulcanizate can absorb as a maximum at a given temperature (25° C). Table I, Column 5, and Table II, Column 5, show the $1/Q_t$ values obtained. To be
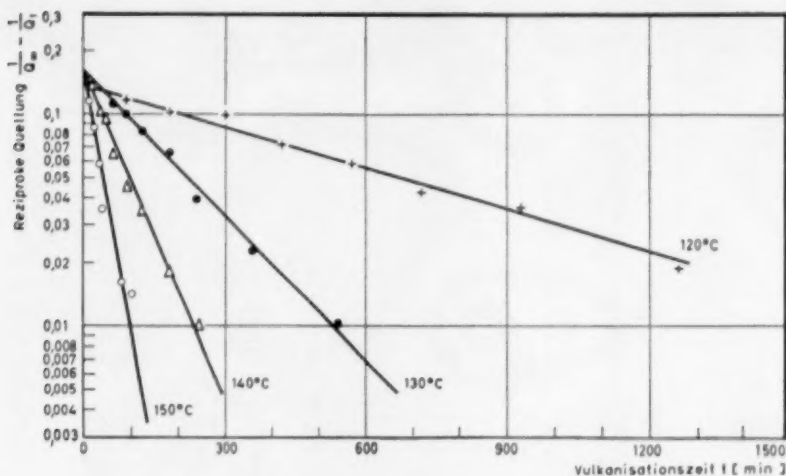
FIG. 6.—The kinetics of reciprocal swelling of sulfur cured natural rubber vulcanizates accelerated with mercaptobenzothiazole in the presence of zinc oxide.   The ordinate is reciprocal swelling and the abscissa cure time.

able to make a kinetic analysis of the variation in swelling, it is necessary to establish the limit value of $1/Q_t$, for $t \rightarrow \infty$  $(1/Q_\infty)$.   For this purpose the log of $1/Q_t$ is plotted against the reciprocal vulcanization time.   From the intercept of the curve so obtained with the ordinate, which can be rather accurately determined, we arrive at $1/Q_\infty$.   We shall not repeat any of those plots here.   It was found, in some cases, that at a vulcanization temperature of 130° C or over, by
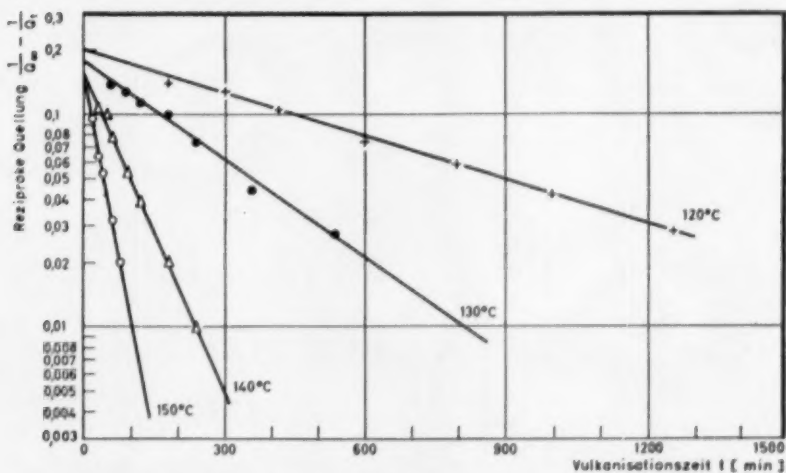


FIG. 7.—The kinetics of reciprocal swelling of sulfur cured natural rubber vulcanizates accelerated with the zinc salt of mercaptobenzothiazole in the presence of zinc oxide.   The ordinate is reciprocal swelling and the abscissa cure time.

## TABLE IV

### VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF ZnO AND SEVERAL CONCENTRATIONS OF ZINC BENZOTHIAZOLYLMERCAPTIDE (ZnM) AT 140° C

Composition of mixture

Mole ratio $S_8$:Zn-M

| 1:0.125 S 3.206 g. ZnO 4.07 g. Zn-M 0.62 g. Rubber 92.104 g. | | | 1:0.25 S 3.206 g. ZnO 4.07 g. Zn-M 1.24 g. Rubber 91.484 g. | | | 1:0.375 S 3.206 g. ZnO 4.07 g. Zn-M 1.86 g. Rubber 90.864 g. | | | 1:0.5 S 3.206 g. ZnO 4.07 g. Zn-M 2.48 g. Rubber 90.244 g. | | | 1:1 S 3.206 g. ZnO 4.07 g. Zn-M 4.96 g. Rubber 87.764 g. | | | 1:1.35 S 3.206 g. ZnO 4.07 g. Zn-M 6.70 g. Rubber 86.024 g. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Vulc. time, minutes | Free S, % | Unreacted accelerator, % | Vulc. time, minutes | Free S, % | Unreacted accelerator, % | Vulc. time, minutes | Free S, % | Unreacted accelerator, % | Vulc. time, minutes | Free S, % | Unreacted accelerator, % | Vulc. time, minutes | Free S, % | Unreacted accelerator, % | Vulc. time, minutes | Free S, % | Unreacted accelerator, % |
| 20 | 86.7 | — | 20 | 83.5 | — | 15 | 81.5 | 95.9 | 15 | 80.5 | 97.0 | 15 | 83.3 | 98.9 | 15 | 87.8 | 99.4 |
| 40 | 72.0 | — | 40 | 71.0 | 82.0 | 30 | 77.4 | 91.7 | 30 | 79.2 | 95.0 | 30 | 61.3 | 97.2 | 30 | 79.2 | 98.8 |
| 60 | 62.1 | 75.3 | 60 | 61.4 | 78.0 | 45 | 63.8 | 88.6 | 45 | 65.6 | 91.5 | 45 | 55.8 | 96.3 | 45 | 68.8 | 98.1 |
| 90 | 46.4 | 65.2 | 75 | 49.2 | 76.7 | 60 | 58.3 | 87.5 | 60 | 57.6 | 89.6 | 60 | 44.9 | 94.9 | 60 | 58.4 | 96.6 |
| 120 | 33.7 | 57.8 | 90 | 44.1 | 74.7 | 90 | 38.4 | 85.3 | 90 | 33.3 | 88.9 | 90 | 32.1 | 91.9 | 90 | 39.9 | 95.2 |
| 180 | 15.4 | 43.1 | 120 | 30.6 | 72.2 | 120 | 28.3 | 79.9 | 120 | 23.2 | 83.3 | 120 | 22.6 | 92.2 | 120 | 29.2 | 94.8 |
| 240 | 6.3 | 37.2 | 180 | 16.0 | 66.2 | 180 | 13.0 | 75.7 | 180 | 10.7 | 81.7 | 180 | 10.8 | 91.5 | 180 | 15.3 | 93.0 |
| 300 | — | 35.7 | 240 | 9.3 | 60.4 | 300 | 4.2 | 75.0 | 240 | 5.0 | 81.0 | 240 | 5.1 | 90.0 | 240 | 7.8 | 92.5 |

applying $1/Q_t$ over the reciprocal vulcanization time, we obtain curves which indicate a more or less distinct maximum, which presumably is based on a reversion of crosslinking.   In such cases we have established $1/Q_\infty$ by extending the rising part of the curve over and beyond the maximum, though such extrapolation may be saddled with a certain error.   May we say in this connection that when investigating variations in swelling of samples vulcanized with thiuram disulfides we observed no reversion, not even at high vulcanizing temperatures, 140° C and over, or at prolonged vulcanization periods.   This throws some light on the chemical reactions upon which reversion is based.   In this case it is apparently not a matter of an oxidation or thermal splitting of C—C bonds because such degradation should occur in the same manner in samples vulcanized with thiuram disulfides.   These are probably formed by S and some S—S bridges[17].   In the case of sulfur vulcanizates, however, they are formed by polysulfide bridges, which, thermally, could be considerably less stable.   A kinetic analysis of the reciprocal swelling data indicates that by applying the log $(1/Q_\infty - 1/Q_t)$ over the reaction time we again obtain lines. Figures 6 and 7 show this for vulcanizates accelerated with mercaptobenzothiazole and its zinc salt.   One can see that even the crosslinking reaction, measured by reciprocal swelling, may be described as a first order reaction. The lines always cut the ordinate at $1/Q_\infty$.   As can be seen in Figures 6 and 7, the $1/Q_\infty$ values in the individual test series differ somewhat, which could occur, primarily, by reason of a nonuniform degree of mixing of the components which make up the mixtures.

A calculation of the rate constants (Table III) from the slope of the curves shows that the crosslinking reaction and the decrease of sulfur are processes having the same speed[18], a notable result.
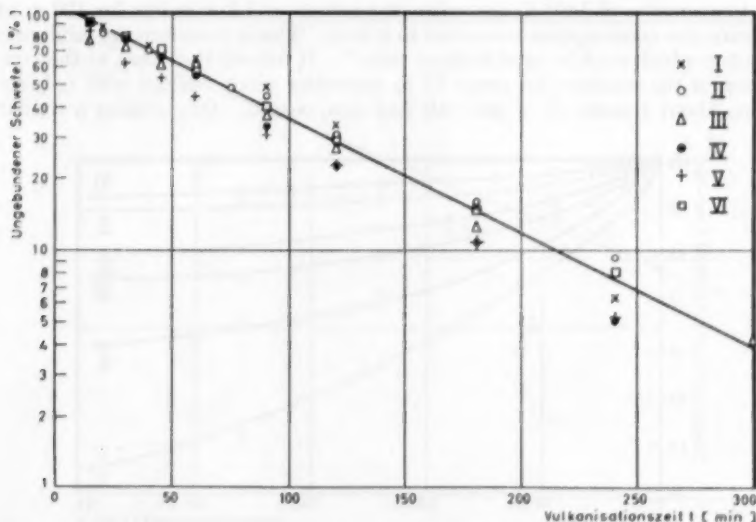


FIG. 8.—The decrease of sulfur as a first order reaction when the zinc salt of mercaptobenzothiazole concentration is varied and with constant concentrations of sulfur and zinc oxide.   The sulfur to zinc salt mole ratios for the various stocks are: *I*, 1 to 0.125; *II*, 1 to 0.25; *III*, 1 to 0.375; *IV*, 1 to 0.5; *V*, 1 to 1; *VI*, 1 to 1.35.

## TABLE V

### RATE CONSTANTS WITH DIFFERENT QUANTITIES OF ACCELERATOR

| Composition of mixture Mole ratio $S_8:M$ | g. Zn-M/ 100 g. | S 3.206 g. ZnO 4.07 g. Zn-M $z$ g. $k_B^I \cdot 10^3$ (min.$^{-1}$) | g. M/100 g. | S 3.206 g. ZnO 4.07 g. Zn-M $z$ g. $k_B^I \cdot 10^3$ (min.$^{-1}$) | $k_B^I \cdot 10^3$ (min.$^{-1}$) |
|---|---|---|---|---|---|
| 1:0.25 | 0.62 | 1.13 | — | — | — |
| 1:0.5 | 1.24 | 1.10 | 1.045 | 0.47 | 0.47 |
| 1:0.75 | 1.86 | 1.16 | — | — | — |
| 1:1 | 2.48 | 1.27 | 2.09 | 0.47 | 0.50 |
| 1:2 | 4.96 | 1.25 | 4.18 | 0.53 | 0.61 |
| 1:2.7 | 6.70 | 1.12 | — | — | — |

*The effects of accelerator concentration.*—To find if the concentration of accelerator affects the kinetics of vulcanization, this was changed, while maintaining the sulfur content constant at 3.2 g. per 100 g. of mixture. In the case of the zinc salt of mercaptobenzothiazole, a series of tests was selected, with the following mole ratios of $S_8$:zinc salt 1:0.125, 1:0.25, 1:0.375, 1:0.5, 1:1, and 1:1.35. The vulcanization temperature was 140° C and the results are shown in Table IV.

Figure 8 shows that the rate constants of sulfur decrease, Table V, Column 3, are independent of the concentration of the accelerator. The points for the individual runs fall on parallel lines but in order to avoid confusion in the overall picture we have drawn only a single line in Figure 8. Figure 9 gives once more the per cent decrease of the accelerator which becomes larger as the amount of the accelerator used is lessened (see Table IV).

It is shown that in all cases the same amount of zinc benzothiazolylmercaptide has been consumed at the conclusion of the reaction. Thus at a vulcanizing temperature of 140° C and with an addition of 3.2 g. sulfur for 100 g. of mixture, the consumption amounted to 0.45 g. This is therefore the minimum quantity which must be used in these tests[19]. It follows then that at the conclusion of the reaction, for every 11 $S_8$ molecules which reacted with polyisoprene, about 1 molecule of zinc salt had disappeared. One obtains a similar
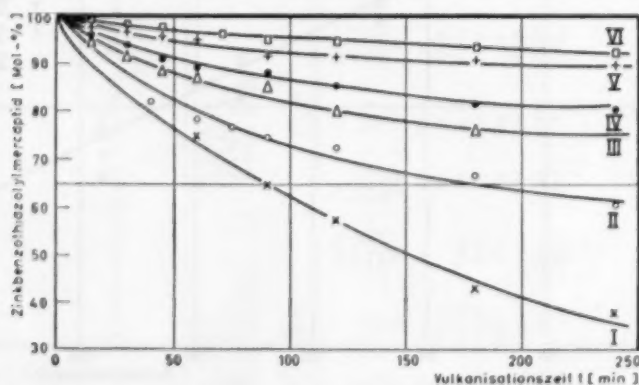


FIG. 9.—The decrease of accelerator concentration with time for various initial concentrations of zinc salt and at constant concentrations of sulfur and zinc oxide. The sulfur to zinc salt mole ratios for the various stocks are: *I*, 1 to 0.125; *II*, 1 to 0.25; *III*, 1 to 0.375; *IV*, 1 to 0.5; *V*, 1 to 1; *VI*, 1 to 1.35.

TABLE VI

VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF ZNO AND
VARIOUS QUANTITIES OF MERCAPTOBENZOTHIAZOLE (M) AT 130° C

Composition of mixture

| S 3.206 g.<br>ZnO 4.07 g.<br>M 1.045 g.<br>Rubber 91.679 g. | | | S 3.206 g.<br>ZnO 4.07 g.<br>M 2.09 g.<br>Rubber 90.634 g. | | | S 3.206 g.<br>ZnO 4.07 g.<br>M 4.18 g.<br>Rubber 88.544 g. | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Mole ratio $S_8$:M | | | | |
| | 1:0.5 | | | 1:1 | | | 1:2 | |
| Vulcanisation time, minutes | Free S, % | $\frac{1}{Q_i}$ | Vulcanisation time, minutes | Free S, % | $\frac{1}{Q_i}$ | Vulcanisation time, minutes | Free S, % | $\frac{1}{Q_i}$ |
| 30 | 82.4 | — | 30 | 80.0 | — | 30 | 82.8 | 0.060 |
| 60 | 70.8 | 0.043 | 60 | 71.2 | 0.0433 | 60 | 68.8 | 0.088 |
| 90 | 62.6 | 0.057 | 90 | 63.0 | 0.055 | 90 | 53.4 | 0.114 |
| 120 | 54.2 | 0.074 | 120 | 54.3 | 0.070 | 120 | 51.5 | 0.124 |
| 180 | 44.8 | 0.101 | 180 | 42.1 | 0.092 | 180 | 38.5 | 0.144 |
| 240 | 34.5 | 0.122 | 240 | 30.1 | 0.116 | 360 | 14.1 | 0.172 |
| 360 | 19.2 | 0.148 | 360 | 15.9 | 0.133 | 480 | 8.5 | 0.180 |
| 480 | 13.2 | 0.160 | 540 | 7.5 | 0.146 | ∞ | | 0.190 |
| ∞ | | 0.183 | ∞ | | 0.156 | | | |

result if, in place of zinc benzothiazolylmercaptide we use an equimolar quantity
of mercaptobenzothiazole in the presence of zinc oxide. Thus Table VI and
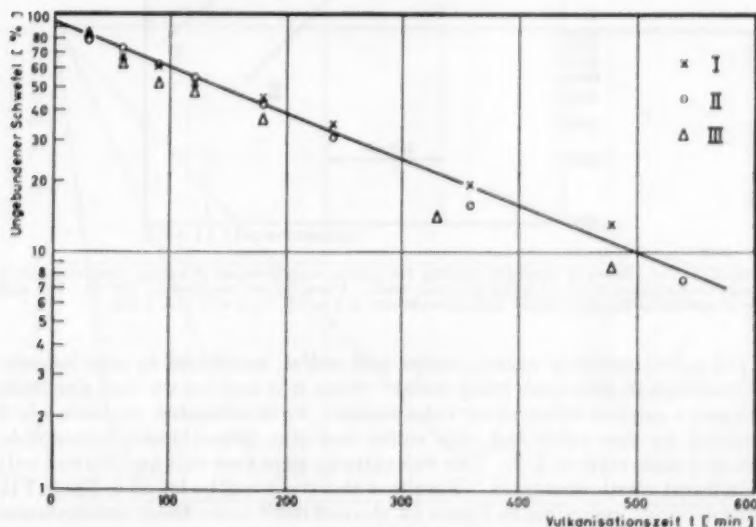Figure 10, show that in this case the rate constant for sulfur decrease does not



FIG. 10.—The decrease of sulfur at 130° C as a first order reaction at various levels of zinc salt concentration but at constant concentration of sulfur and zinc oxide. The mole ratios of sulfur to zinc salt concentration for the various stocks are: *I*, 1 to 0.5; *II*, 1 to 1; *III*, 1 to 2.

change the mole ratios examined by us—$S_8$:mercaptobenzothiazole = 1:0.5, 1:1 and 1:2 (Table V, Column 5).

We then tested the rate of network formation as a function of the concentration of accelerator. In Figure 11 is shown the reciprocal swelling of the vulcanizates in the three runs with varying contents of mercaptobenzothiazole, as a reaction of first order. The curves running approximately parallel indicate that the speed of network formation is not affected by the concentration of accelerator. Also, the maximum degree of netting, for which $1/Q_\infty$ is the measure, is not sensibly affected by an increased amount of accelerator.
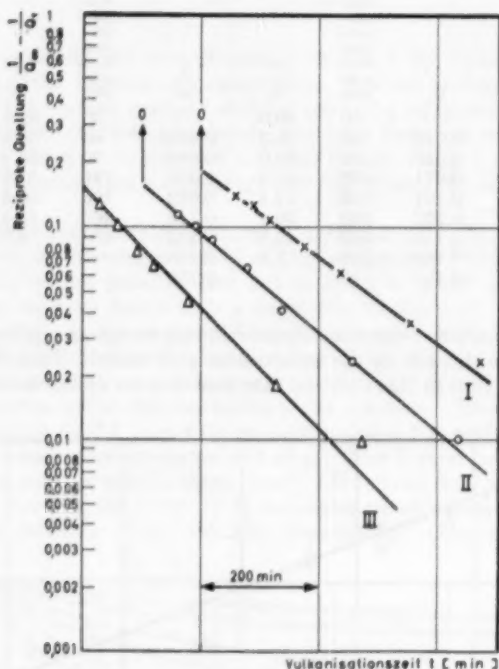


Fig. 11.—The kinetics of reciprocal swelling for various concentrations of mercaptobenzothiazole at constant concentration levels of sulfur and zinc oxide. Vulcanization temperature 130° C. The mole ratios of accelerator to sulfur for the various stocks are: I, 1 to 0.5; II, 1 to 1; III, 1 to 2.

*The vulcanization of natural rubber with sulfur, accelerated by zinc benzothiazolylmercaptide, zinc oxide being absent.*—Since it is well known that zinc oxide often has a marked influence on vulcanization, we investigated mixtures which contained no zinc oxide but only sulfur and zinc benzothiazolylmercaptide, again in a mole ratio of 2:1. The vulcanizates were very soft and showed only insignificant elastic character. Results of this study will be found in Table VII. Sulfur decrease, according to Figure 12, showed itself under these circumstances to be a first order reaction. It should be noted, however, that the rate constants $k_S{}^I$ are about 2.5 times as large as those of the sulfur decrease in the corresponding vulcanizates which contain zinc oxide. The reaction of sulfur with

## TABLE VII

### VULCANIZATION OF NATURAL RUBBER WITH SULFUR IN THE PRESENCE OF ZINC BENZOTHIAZOLYLMERCAPTIDE (ZnO BEING ABSENT)

Composition of mixture:

Sulfur 3.206 g. (0.1 gram atom)
Zinc Benzothiazolylmercaptide 2.48 g. (0.00625 mole)
Rubber 94.314 g.

| 110° C | | | 120° C | | | 130° C | | | 140° C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Vulcanisation time, minutes | Free S % | $\frac{1}{Q_i}$ | Vulcanisation time, minutes | Free S % | $\frac{1}{Q_i}$ | Vulcanisation time, minutes | Free S % | $\frac{1}{Q_i}$ | Vulcanisation time, minutes | Free S % | $\frac{1}{Q_i}$ |
| 110 | 85.5 | 0.0435 | 90 | 67.2 | 0.071 | 30 | 82.2 | — | 10 | 82.9 | — |
| 400 | 54.8 | 0.0797 | 180 | 43.2 | 0.1043 | 60 | 63.7 | — | 15 | 70.2 | 0.0547 |
| 750 | 26.0 | 0.108 | 300 | 22.7 | 0.1226 | 90 | 48.4 | 0.064 | 20 | 63.7 | 0.078 |
| 1000 | 19.6 | 0.124 | 420 | 11.0 | 0.1279 | 120 | 35.6 | 0.077 | 30 | 45.8 | 0.111 |
| 1400 | 9.6 | 0.128 | 620 | 5.6 | 0.1182 | 180 | 20.2 | 0.091 | 40 | 34.7 | 0.123 |
| 1800 | 4.0 | 0.130 | 800 | 3.3 | — | 240 | 11.4 | 0.082 | 60 | 21.0 | 0.1278 |
| 3020 | 1.1 | 0.116 | 1015 | 1.5 | 0.1111 | 360 | 4.1 | 0.073 | 90 | 8.1 | 0.1190 |
| 4400 | — | 0.108 | 1250 | — | 0.1072 | 540 | — | 0.044 | 120 | 3.9 | 0.1042 |
| | | | | | | | | | 180 | — | 0.0968 |

rubber, therefore, proceeds considerably faster in the absence of zinc oxide. From the dependence on temperature of the rate constants, Figure 3, Curve *II*, we calculate an activation energy of 29.5 kcal./mole. We obtain practically the same value as from vulcanizates containing zinc oxide, see Figure 3, Curve *I*. The measured swelling, $Q_i$, on the other hand, was considerably larger than that shown by corresponding vulcanizates containing zinc oxide. In addition,
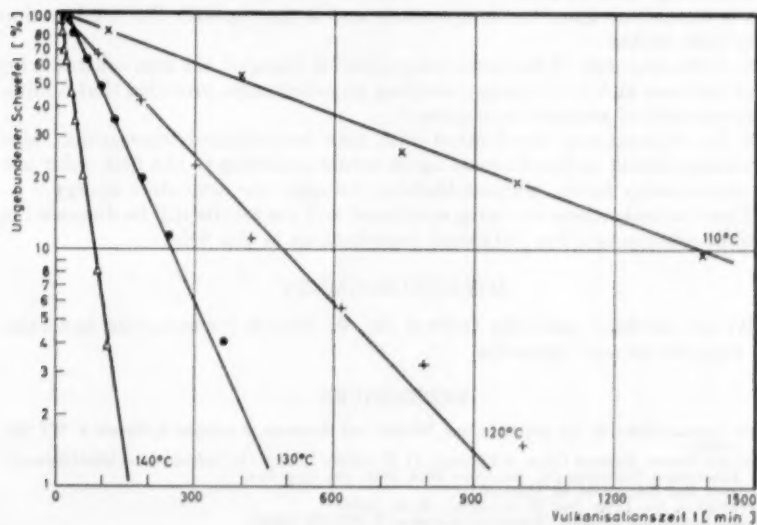


FIG. 12.—The decrease of sulfur as a first order reaction for the sulfur vulcanization of natural rubber with the zinc salt of mercaptobenzothiazole as the accelerator in the absence of zinc oxide.

considerable reversion occurred. Since this was noticeable at all temperatures, an evaluation of the reaction kinetics could not be made. The circumstances point to the fact that in the absence of zinc oxide there are very likely fewer crosslinks created and their nature will depend to a great extent on whether zinc oxide is present in the mixture or not because, in the absence of zinc oxide, it appears that the union of macromolecules of the rubber occurs primarily through links which, thermally, are extremely unstable. Some experiences would indicate that we are dealing here with polysulfide bridges 20.

No matter what the individual circumstances may be, the present findings show in any case, for sulfur vulcanization accelerated by mercaptobenzothiazole or zinc benzothiazolylmercaptide, that zinc oxide plays an important role in the selective direction of the reaction, with respect to nature and structure of the crosslinks[21].

## SUMMARY

1. The decrease of free sulfur occurs according to the first order law during the vulcanization of natural rubber accelerated by mercaptobenzothiazole in the presence of zinc oxide. The activating energy for this reaction amounts to 30.5 kcal./mole.

2. If zinc benzothiazolylmercaptide is used as an accelerator, one obtains the same rate constants for the sulfur decrease as in the presence of mercapto-benzothiazole. These seem to be equivalent as regards their effectiveness of acceleration.

3. A kinetic analysis of the reciprocal swelling, which represents a measure of network formation, indicates that the reaction is first order. Sulfur decrease and reciprocal swelling prove to be equal processes as regards rate. This is true where vulcanization is accelerated with mercaptobenzothiazole or with the zinc salt.

4. During vulcanization there occurs a decrease of accelerator concentration. This is dependent upon the temperature and is tied in with the combination sulfur with rubber.

5. If the quantity of the accelerator added is changed, the rate constants for sulfur decrease and for reciprocal swelling do not change, provided that a minimum quantity of accelerator is present.

6. In vulcanization accelerated with zinc benzothiazolylmercaptide, zinc oxide being absent, sulfur decrease again occurs according to the first order law but considerably faster, without thereby changing the activation energy.

These investigations are being continued and the results will be discussed in detail in relation to other published contributions in this field.

## ACKNOWLEDGMENT

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6 Lorenz and Echte, *Kautschuk u. Gummi* 9, WT 300 (1956).
7 Compare with Reference 1.
8 For the details of this analysis see Reference 6.

[9] Auerbach, Reference 3, also observed in his tests with GR-S approximately the same rate constants for vulcanization accelerated with mercaptobenzothiazole or its zinc salt, respectively.

[10] As something of a contradiction to the assumption that zinc benzothiazolylmercaptide is the actual accelerator we mention the following experimental result: If we use mercaptobenzothiazole as the accelerator, we observe a preliminary reaction, because in Figure 1 the curves do not cut the ordinate at 8 = 100 (per cent of the amount added) but rather at 90 and 95. On the other hand, if the mixtures contain zinc benzothiazolylmercaptide as the accelerator, this is not observed and instead, in some cases, even a short induction period occurs (see Figure 2). Further tests will be needed to clarify this point.

[11] Spence and Young, Kolloid-Z. 11, 28 (1912).

[12] This value was confirmed in tests (still unpublished) made by W. Scheele and M. Cherubim.

[13] Gordon, J. Polymer Sci. 7, 485 (1951).

[14] Zapp, Decker, Dyroff, and Rayner, J. Polymer Science 6, 331 (1950).

[15] Farmer in "Advances of Colloid Science", Interscience Publishing Co., New York, 1946, Vol. II, p. 349.

[16] Dogadkin and coworkers, RUBBER CHEM. & TECHNOL. 29, 917 (1956).

[17] Dogadkin, Tarasova, RUBBER CHEM. & TECHNOL. 26, 759 (1953). Bielstein and Scheele, Kolloid-Z. 147, 152 (1956).

[18] This is true, however, only of vulcanizates containing sulfur, zinc oxide and mercaptobenzothiazole or its zinc salt. It was found that in the presence of zinc salts of fatty acids the crosslinking reaction and the sulfur decrease are no longer processes having the same speed. We shall shortly give a further report on this.

[19] At different temperatures one obviously applies also different minimum quantities of accelerator, which have to be determined separately in each case. Compare the dependence on temperature of the decrease of accelerator concentration, from which such figures are obtained.

[20] Dogadkin and Tarasova, Reference 17.

[21] See in this connection the summary on the effect of zinc oxide presented by E. H. Farmer in Reference 2, page 355.

# DEGREE OF CURE IN FILLER-REINFORCED VULCANIZATES BY THE SWELLING METHOD *

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The physical properties of a rubber vulcanizate depend mainly on three factors: the chemical constitution and physical structure of the polymer; the type and degree of crosslinking; and the reinforcement by fillers. It is now widely recognized that these factors are by no means independent of each other. Thus, the chemical nature of the polymer obviously determines the type of crosslinkages which can be introduced into the rubber. Fillers contribute to crosslinking by adsorption of the polymer molecules on their surface and appear capable of modifying the course and efficiency of vulcanization reactions either directly or through adsorption of curatives.

This complex and delicate interplay of chemical reactions and physical phenomena complicates the very definition of such quantities as degree of vulcanization or state of cure in a filler-reinforced vulcanizate. Are effective crosslinks due to adsorption by the filler to be counted as contributing to the degree of vulcanization? If not, then how can the two types of linkages be distinguished from each other? It seems that the answer to these questions can best be provided by the physical properties of the vulcanizate itself or, more specifically, by their response to changes in the variable chosen as representative of the degree of cure.

It is apparent that the degree of vulcanization must be identified with some variable characteristic of the number of crosslinks introduced. It should also take cognizance of the fact that a network formed from low molecular weight polymer will require a greater number of crosslinks for its formation than one formed from high molecular weight rubber. This fact suggests the number of effective network chains per unit volume of rubber (or its reciprocal, the molar volume of a network chain) as a suitable measure of vulcanization. This quantity is not only a logical choice, but one which offers very little difficulty toward its measurement.

For a gum vulcanizate it can be determined with little ambiguity from equilibrium modulus or swelling data by means of the statistical network theory of rubber elasticity and the thermodynamics of swelling[1]. If this same quantity is chosen as criterion for the degree of vulcanization of a filler-reinforced stock, then the filler will clearly exert an effect on the result. It will be shown that regardless of the nature of the apparent filler contribution it is desirable to have the filler effect included in the "degree of cure."

In gum stocks it makes little difference whether the number of effective network chains is ascertained from swelling or modulus data; with filler-reinforced stocks the swelling technique offers decided advantages. The difficulties

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associated with the determination of equilibrium moduli for any vulcanizate are several. When the sample is stretched to a fixed elongation, the stress decays very slowly, apparently without reaching an equilibrium value[2].

This difficulty can be overcome by first prestretching the specimen to a higher elongation[3], but even then the total amount of time necessary to obtain an equilibrium value is of the order of hours. Another method is to swell the specimen in the vapor of a solvent while under stress and then dry the specimen in situ[2], a procedure hardly conducive to routine testing. In filled stocks there is the additional complication due to the well-known Mullins[4] effect if the prestretching method is employed; deviations from the simple kinetic theory stress-strain relation are also more pronounced than in gum stocks.

Satisfactory equilibrium moduli can be obtained rapidly by measurements on fully swollen gum stocks[2,5,6]. This method can be adapted to filler-reinforced elastomers by also prestretching the sample. In this instance, however, knowledge of the swelling volume is also required so that the measurement of the modulus becomes redundant provided the necessary solubility relations are known for the polymer. In the present work the approach chosen was to develop these relations from data on gum stocks and to rely on swelling measurements alone for the determination of the density of effective network chains in all vulcanizates including those containing reinforcing fillers.

## THEORETICAL ASPECTS

*The number of effective network chains per unit volume of rubber* ($\nu$) is given in terms of swelling volume by the well-known Flory-Rehner[7,8] equation

$$\nu = -\frac{1}{V_s} \cdot \frac{\ln(1 - v_r) + v_r + \mu v_r^2}{v_r^{\frac{1}{3}} - \frac{2v_r}{f}} \tag{1}$$

where $V_r$ *is the volume fraction of rubber in the swollen network,* $V_s$ *is the molal volume of the solvent,* $f$ *is the functionality of the cross-links, and* $\mu$ *is the Huggins solubility parameter.* (The notation differs significantly from that of Flory only in that $\nu$ is referred to *unit volume.*) When the network is formed in the presence of diluent such as is the case in oil-extended rubbers, Equation 1 takes the form

$$\nu' = -\frac{1}{V_s} \cdot \frac{\ln(1 - v_r) + v_r + \mu v_r^2}{v_r^{\frac{1}{3}} v_0^{\frac{2}{3}} - \frac{2v_r}{f}} \tag{2}$$

where $V_0$ *is the volume fraction of network rubber in the original stock, and* $\nu'$ *is now the density of network chains based on the extracted volume*[9]. For most purposes, however, the desired $\nu$ will be one that is based on the unextracted volume; hence,

$$\nu = v_0 \nu' = -\frac{v_0}{V_s} \cdot \frac{\ln(1 - v_r) + v_r + \mu v_r^2}{v_r^{\frac{1}{3}} v_0^{\frac{2}{3}} - \frac{2v_r}{f}} \tag{3}$$

Since synthetic emulsion polymers usually contain some 5% to 7% of fatty acid and soap, Equation 3 should, strictly speaking, be used at all times. Unless $v_0$ is smaller than 0.80, however, the difference will be trivial so that in

practice it is only necessary to resort to the more complicated Equation 3 for oil-extended rubbers.

The solubility parameter $\mu$ can be found conveniently by a slight modification of Gee's[10] method. The stress-strain relation for a swollen rubber is

$$F/A = \nu'RTv_r^{\frac{1}{3}}\left(\alpha - \frac{1}{\alpha^2}\right)$$ (4)

where *F is the force of retraction at extension ratio a, A is the cross-sectional area of the swollen specimen, R is the gas constant, and T is the absolute temperature.* Solving Equations 2 and 4 simultaneously yields the desired solubility parameter $\mu$. This parameter is, in general, a function of concentration, i.e., $v_r$. For good solvents the variation of $\mu$ with concentration is slight, but for poor solvents it is appreciable. For all rubber-solvent pairs studied here, the relation could be represented by a linear function of $v_r$ (Table I)

$$\mu = \mu_0 + \beta v_r$$ (5)

where *$\beta$ is a constant characteristic of the rubber-solvent system.*

The last column of Table I allows a comparison with literature values derived from colligative properties of polymer solutions. Since these values were determined in dilute solutions, the comparison should be with $\mu_0$. The agreement must be regarded as good particularly since not all of the polymers are exactly the same. The $\mu$ for the system natural rubber-benzene increases slightly with $v_r$, but the vapor pressure measurements of Gee[11] showed it to be independent of concentration. It must be remembered, however, that the crosslinked rubbers used in this determination contain increasing amounts of

TABLE I

SOLUBILITY PARAMETERS

| Rubber | Solvent | Temp., °C | $\mu_0$ | $\beta$ | Literature $\mu$ |
|---|---|---|---|---|---|
| Styrene-butadiene-rubber (SBR)[1] (cold rubber, 23.5% bound styrene) | n-heptane | 30 | 0.47 | 0.39 | — |
| | benzene | 30 | 0.37 | 0.27 | 0.37[a] |
| Hevea (No. 1 RSS) | n-heptane | 30 | 0.46 | 0.20 | — |
| | toluene | 30 | 0.43 | 0.05 | 0.41[b], 0.43[c] |
| | benzene | 25 | 0.44 | 0.18 | 0.44[c] |
| Butyl (Enjay Butyl 217) | n-heptane | 30 | 0.46 | 0.26 | — |
| | benzene | 25 | 0.51 | 0.35 | 0.50[d] |
| | cyclohexane | 25 | 0.44 | 0.17 | 0.43[d] |
| Butadiene-2-methyl-5-vinylpyridine copolymer[2], sulfur cured | benzene | 30 | 0.41 | 0.10 | — |
| Butadiene-2-methyl-5-vinylpyridine copolymer[2], benzo-trichloride cured | benzene | 30 | 0.42 | 0.54 | — |

[1] Philprene 1500 (registered trade mark of Phillips Petroleum Co.).
[2] Philprene VP-25.
[a] At 25° C, Zimm and Myerson, *J. Am. Chem. Soc.* **68**, 911 (1946).
[b] Carter, Scott and Magat, *J. Am. Chem. Soc.* **68**, 1480 (1946).
[c] Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).
[d] Polyisobutylene; Flory, *J. Am. Chem. Soc.* **65**, 375 (1943).

combined sulfur, the tendency of which could be to raise $\mu$ in hydrocarbon solvents because of a slight increase in cohesive energy density of the network over the unvulcanized, linear polymer.

To determine $\nu$ for a filler-reinforced stock, $v_r$ is calculated from the swelling data on the assumption that the filler does not swell. The resulting value of $v_r$ is then substituted in Equation 1 or 3, using the value of $\mu$ given by Equation 5. This procedure assumes that $\mu$ will not be affected by the filler. In view of the short range of molecular forces this assumption does not appear unreasonable. A simple calculation shows that with a filler of 25 millimicrons diameter at a loading of 20 volume per cent, only 6.5 per cent of the polymer is situated within a 10 Å layer of the filler surface. Therefore the effect on solubility must be relatively small. What effect there might be will, of course, be absorbed in the value calculated for $\nu$.

## EXPERIMENTAL

*Swelling measurements.*—Samples of vulcanized rubber weighing approximately 1.5 grams were cut from regular tensile slabs, weighed on an analytical balance, and allowed to swell in 100 milliliters of the desired solvent for six days at 30° C (see section on standardization of procedure). As a precaution against oxidation, 0.2% of phenyl-2-naphthylamine was added to the solvent. The swollen specimens were blotted with filter paper and transferred quickly to tared weighing bottles. The volume of imbibed solvent was obtained by dividing the difference between the weight of the swollen sample and the weight of the dry, extracted sample (dried 16 hours at 70° C in vacuo) by the density of the solvent. Next the dry samples were weighed in methanol, and their volume calculated. From this volume was subtracted the volume of fillers (calculated from the recipe and original sample weight) giving the volume of rubber. The latter was used to calculate the volume fraction of rubber in the swollen polymer ($v_r$).

All solvents employed were either reagent grade or Phillips pure grade (minimum 99 mole per cent purity).

*Modulus determinations on swollen gum stocks.*—The procedure employed in determining the values of the solubility parameter $\mu$ was as follows. A set of gum stocks of variable degree of cure was prepared, and samples were analyzed for swelling volume, as described above. In addition, regular dumbbell tensile specimens were swelled to their equilibrium value. The swollen dumbbells were prestretched to 150% elongation on an Instron tester, and a stress-strain curve was determined at decreasing elongations, using a crosshead speed of five inches per minute. The force of retraction at 50% elongation was used in the calculation of $\mu$ from Equations 2 and 4.

As a result of the combination of swelling and prestretching, this procedure gives a modulus which is very nearly an equilibrium value. Because of the low temperature and short duration of the experiment, chemo-rheological effects are absent. Hysteresis effects are nevertheless small, and there is essentially no permanent set. Unless extremely volatile solvents are used, evaporation of solvent from the specimen during the test is not a serious problem. Errors introduced from this source are inappreciable because of the slow (cube root) dependence of the retractive force on swelling volume.

*Compounding recipes.*—Space does not permit listing all the recipes for the stocks employed in this study. The most important ones are listed in Table II. Gum stock formulations designed for determinations of $\mu$ values were kept

## TABLE II

### Compounding Recipes[1]

| | A | B | C | D | E | F | G | H | I | J | K | L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cold styrene–butadiene rubber (SBR) (23.5% bound styrene)[2] | 100 | 100 | 100 | — | 100 | 100 | — | 100 | 100 | 100 | 100 | 100 |
| No. 1 RSS | — | — | — | — | — | — | — | — | — | — | — | — |
| Butyl rubber[3] | — | — | — | — | — | — | 100 | — | — | — | — | — |
| Butadiene-2-methyl-5-vinyl-pyridine copolymer (75/25), 41°F, ML-4, 50[4] | — | — | — | — | — | — | — | — | — | — | — | — |
| Other polymer | — | — | — | — | — | — | — | — | — | — | — | — |
| HAF carbon black[5] | 42 | 50 | 50 | — | — | — | — | — | — | — | — | — |
| SAF carbon black[6] | — | — | — | V | — | — | — | 50 | 50 | 50 | 50 | 50 |
| Other carbon black | — | — | — | V | — | — | — | — | — | — | — | — |
| Hydrated silica pigment[7] | — | — | — | V | — | — | — | — | — | — | — | — |
| Highly aromatic petroleum oil[8] | — | — | — | — | V | V | V | — | V | — | — | — |
| Naphthenic oil and asphaltic flux product[9] | — | — | — | — | — | — | — | — | — | — | — | — |
| Zinc oxide | 4 | 5 | 3 | 3 | 3 | 4 | 5 | 5 | — | — | 5 | 5 |
| Stearic acid | 3 | 3 | 1 | 1 | — | 3 | 1 | 2 | — | — | — | — |
| Sulfur | 2 | 1 | 1.75 | 2.25 | 1.75 | 2 | 2 | V | — | — | 1.75 | 5 |
| N-cyclohexyl-2-benzothiazole sulfenamide[10] | V | 1.75 | 1.0 | 1.25 | 1.10 | 0.5 | 1 | V | — | — | — | — |
| Tetramethylthiuram disulfide[11] | V | — | — | — | — | — | 1 | V | — | — | 0.65 | — |
| Mercaptobenzothiazole[12] | — | — | — | — | — | — | — | — | — | — | — | — |
| tert-Butyl-sulfenyl dimethyldithiocarbamate[13] | — | — | — | — | — | — | — | — | — | — | — | — |
| Other accelerator | — | V | — | — | — | — | — | — | V | — | — | — |
| Dicumyl peroxide | — | — | — | — | — | — | — | — | — | — | — | — |
| Benzotrichloride | — | — | — | — | — | — | — | — | — | — | — | — |
| Diarylamine-ketone reaction product 65%, N,N'-diphenyl-p-phenylene-diamine 35%[14] | 1 | 1 | 1 | 1 | — | — | — | — | — | — | — | 20 |
| Phenyl-2-naphthylamine | — | — | — | — | — | — | — | 1.5 | — | — | — | — |

[1] Entries termed V (variable) are as indicated in text. Gum stocks referred to in text are identical with recipes as shown except for omission of reinforcing agent.
[2] Philprene 1500.
[3] Enjay Butyl 217 (Enjay Co., Inc., New York, N. Y.).
[4] Philprene VP-25.
[5] Philblack O (registered trade mark of Phillips Chemical Co., Akron, O.).
[6] Philblack E (registered trade mark of Phillips Chemical Co., Pittsburgh, Pa.).
[7] Hi-Sil 101 (Columbia-Southern Chemical Corp., Pittsburgh, Pa.).
[8] Philrich 5 (registered trade mark of Phillips Chemical Co.).
[9] Circo-Para (50 parts Circosol 2 XH, Sun Oil Co., Philadelphia, Pa.; 50 parts Paraflux 2016, C. P. Hall Co., Akron).
[10] Santocure (Monsanto Chemical Co., Akron).
[11] Tuads (R. T. Vanderbilt Co., Inc., New York).
[12] Captax (R. T. Vanderbilt Co., Inc.).
[13] Philcure 113 (registered trade mark Phillips Petroleum Co.).
[14] Flexamine (Naugatuck Chemical Division, United States Rubber Co., Naugatuck, Conn.).

TABLE III

CARBON BLACK PROPERTIES

| Name | Type | Surface area (sq. m./g.) | | | Ultimate analysis (%) | | | | |
| | | BET[6] | Electron micro- scope | Oil ab- sorption, cc./g. | C | H | O | S | Ash |
|---|---|---|---|---|---|---|---|---|---|
| P-33[1] | FT | 13.7 | 17 | 0.56 | 99.22 | 0.48 | 0.24 | 0.00 | 0.06 |
| Gastex[2] | SRF | 27.6 | 35 | 0.81 | 97.52 | 0.32 | 0.42 | 0.09 | 1.65 |
| Philblack A[3] | FEF | 45.6 | 65 | 1.17 | 98.44 | 0.32 | 0.38 | 0.68 | 0.18 |
| Philblack O[3] | HAF | 75.1 | 94 | 1.14 | 98.22 | 0.30 | 0.83 | 0.41 | 0.24 |
| Philblack E[3] | SAF | 142.6 | 138 | 1.28 | 97.31 | 0.33 | 1.69 | 0.43 | 0.24 |
| Acetylene | — | 58.0 | 65 | 2.40 | 99.78 | 0.07 | 0.07 | 0.03 | 0.05 |
| Wyex[4] | EPC | 114.2 | 89 | 1.13 | 95.84 | 0.71 | 3.40 | 0.02 | 0.03 |
| Graphon[5] | C | 93.7 | 113 | 1.13 | 98.47 | 0.02 | 0.12 | 0.02 | 1.37 |

[1] R. T. Vanderbilt Co., Inc.
[2] General Atlas Division, Cabot Carbon Co., Pampa, Tex.
[3] Phillips Chemical Co.
[4] J. M. Huber Corp., New York.
[5] Godfrey L. Cabot, Inc., Boston, Mass.
[6] Brunauer, Emmett, and Teller method.

as simple as possible with neither softeners nor additional antioxidant employed. The carbon blacks were from the identical lots used in earlier studies[12,13]; a summary of their physical and chemical properties is shown in Table III.

*Physical testing.*—The following standard test procedures were employed in the determination of vulcanizate physical properties:

(a) *Abrasion loss*: Goodyear-Huber angle abrader, wheel angle 15 degrees. Results expressed in grams loss. Alternate method: National Bureau of Standards abrader with No. 2½ Garnet paper. Specimens for NBS abrasions were extracted with the azeotropic mixture of ethanol and toluene. Results expressed in revolutions per mil abraded (ASTM D394-47).

(b) *Resilience*: Yerzley oscillograph (ASTM D945-55 with slightly modified specimen).

(c) *Heat buildup*: Goodrich flexometer; results expressed in degrees F (ASTM D623-52T, Method A; 143 psi, 0.175-inch stroke, 100° F oven).

(d) *Flex life*: De Mattia; results in multiples of 1,000 cycles to failure at 210° F (similar to ASTM D813-52T).

DEVELOPMENT OF A STANDARD SET OF TEST CONDITIONS

*Choice of solvent.*—According to the theory, the number of effective network chains calculated by Equations 1 or 3 should be independent of the solvent provided the values of the solubility parameter appropriate to each solvent and $v_r$ have been used. Table IV shows a test of this hypothesis, using a series of cold rubber stocks reinforced by various carbon blacks.

The agreement between results obtained in benzene and n-heptane is good considering the large disparity in solvent power as indicated by the marked differences in the swelling values ($v_r$). In spite of the fact that benzene is the better solvent for most rubbers (particularly SBR), n-heptane was selected as the standard in this investigation. The reason for this choice was that excessive swelling, such as might be obtained on lightly cured stocks in benzene, is not desirable from the practical viewpoint of handling the samples. With n-heptane the swelling volume for most useful vulcanizates of SBR, Hevea, or butyl rubbers will usually fall into the range of $v_r$ from 0.25 to 0.50. There is, of course, no basic objection to the use of benzene or any other non-polar solvent

TABLE IV

DENSITY OF NETWORK CHAINS CALCULATED FROM SWELLING
DATA IN BENZENE AND $n$-HEPTANE[1]

| Black | Benzene | | $n$-Heptane | |
|---|---|---|---|---|
| | $v_r$ | $\nu \times 10^4$, moles/cc. | $v_r$ | $\nu \times 10^4$, moles/cc. |
| P-33 (FT) | 0.177 | 1.12 | 0.399 | 1.31 |
| Gastex (SRF) | 0.204 | 1.49 | 0.413 | 1.50 |
| Philblack A (FEF) | 0.221 | 1.74 | 0.425 | 1.60 |
| Philblack O (HAF) | 0.217 | 1.67 | 0.417 | 1.56 |
| Philblack E (SAF) | 0.222 | 1.76 | 0.430 | 1.76 |
| Wyex (EPC) | 0.199 | 1.41 | 0.424 | 1.67 |
| Acetylene | 0.225 | 1.80 | 0.441 | 1.93 |
| Graphon (C) | 0.175 | 1.09 | 0.396 | 1.27 |

[1] Cold SBR (Philprene 1500) stocks containing 50 phr of indicated carbon black (Recipe E).   Cured 45 minutes at 307° F.

of reasonably good solvent power.    Unless specifically indicated, all swelling values reported in this paper are for $n$-heptane at 30° C.

*Degradation of polymer during test.*—Inspection of Table IV reveals values of $\nu$ obtained from swelling data in $n$-heptane to be slightly larger on the average than those calculated from benzene data.   Barring deviations from the theory, this would suggest the possibility of degradation of the rubber in the better solvent or perhaps an increased tendency toward disentanglement of free chain ends.   To determine if degradation by chain scission was involved, samples of SBR gum and black vulcanizates were first swollen in benzene for six days, dried, and subsequently swelled in $n$-heptane for six days.   The results were compared with those obtained from simple swelling measurement in $n$-heptane:

| | $v_r$ ($n$-Heptane) | |
|---|---|---|
| | Preswelled in benzene | Not preswelled |
| Gum stock | 0.372 | 0.373 |
| Black stock | 0.404 | 0.404 |

There is no evidence of degradation, and the small differences in the values of $\nu$ obtained in the two solvents must be explained by deviations from theory or more nearly complete disentanglement of chain ends in benzene, the better solvent.   Entanglements trapped between crosslinks should have essentially the same effect in either solvent and would be counted as true crosslinkages.

*Choice of swelling time.*—A swelling time of six days was chosen on the basis of test results on several samples which showed no significant changes after four days of immersion in $n$-heptane.   In some instances an apparent equilibrium $v_r$ was reached in about two days, but the amount of extractable matter removed from the sample was short of its equilibrium value.

The results quoted in Table V are for a SBR-HAF black (Philprene 1500-

TABLE V

EFFECT OF TIME ON SWELLING IN $n$-HEPTANE AT 30° C

| | Hours immersion in $n$-heptane | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | 4 | 8 | 16 | 24 | 48 | 96 | 120 | 144 |
| $v_r$ | 0.427 | 0.426 | 0.422 | 0.421 | 0.419 | 0.419 | 0.423 | 0.4235 | 0.4235 |
| % extracted | 4.3 | 4.9 | 5.1 | 5.6 | 5.7 | 6.1 | 6.4 | 6.5 | 6.5 |

Philblack O) tread stock (Recipe C, Table II) of 25-mil sample thickness; with thicker specimens the approach to equilibrium would, of course, be slower. Procedures for hastening the attainment of equilibrium were also investigated. It was found that quite reliable 30° C values can be obtained by swelling the samples for two hours at 60° C followed by three hours at 30° C.

## RESULTS AND DISCUSSION

*Effects of sulfur and accelerator level on crosslinking at fixed black loading.—* Carbon blacks are often considered to "activate the cure" of elastomeric compounds. The mechanism of this action is not clear, and it is not known to what extent adsorption of polymer chains or segments on the filler surface contributes fixed points to the network which will act very much like crosslinks. The latter type of linkage, which is intimately connected with the effect of reinforcement, might be expected to influence the physical properties of the stock in a manner different from the polymer-to-polymer linkage of vulcanization. As already mentioned, when the number of network chains in a black stock is determined from swelling data, the result will include the contribution of all types of linkages and will, in fact, represent the number of effective network chains in an equivalent network of tetrafunctional crosslinks.

It turns out that at fixed carbon black type and loading almost all important vulcanizate properties with the exception of tensile strength, which is sensitive to the sulfur level, depend in the first approximation on this quantity. They are independent of the manner in which the particular number of effective crosslinks is introduced, whether through variations in sulfur level, accelerator level, or cure time. These observations are illustrated in Table VI and Figures 1 to 3 on a series of cold rubber stocks containing 42 phr of SAF black.

### TABLE VI

#### CROSSLINKING AS A FUNCTION OF CURATIVE LEVEL IN SBR[1]—SAF BLACK[2] STOCKS[3]

| Stock | Sulfur (phr) | N-cyclo-hexyl-2-benzo-thiazole sulfen-amide[4] (phr) | Br | | | | | $\nu \times 10^4$, moles/cc. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cure time, minutes | | | | | | | | | |
| | | | 10 | 20 | 30 | 45 | 75 | 10 | 20 | 30 | 45 | 75 |
| Black | 1.25 | 0.75 | 0.193 | 0.311 | 0.350 | 0.371 | 0.388 | 0.16 | 0.55 | 0.83 | 1.01 | 1.18 |
| | 1.25 | 1.00 | 0.235 | 0.357 | 0.383 | 0.398 | 0.401 | 0.25 | 0.89 | 1.12 | 1.30 | 1.34 |
| | 1.25 | 1.25 | 0.301 | 0.383 | 0.403 | 0.406 | 0.406 | 0.49 | 1.13 | 1.36 | 1.40 | 1.40 |
| | 1.25 | 1.50 | 0.335 | 0.398 | 0.411 | 0.411 | 0.409 | 0.71 | 1.30 | 1.47 | 1.47 | 1.45 |
| Black | 1.50 | 0.75 | 0.193 | 0.341 | 0.378 | 0.398 | 0.409 | 0.16 | 0.75 | 1.07 | 1.29 | 1.44 |
| | 1.50 | 1.00 | 0.275 | 0.381 | 0.403 | 0.415 | 0.417 | 0.38 | 1.11 | 1.36 | 1.54 | 1.56 |
| | 1.50 | 1.25 | 0.333 | 0.404 | 0.419 | 0.423 | 0.424 | 0.69 | 1.38 | 1.60 | 1.66 | 1.67 |
| Black | 1.75 | 0.75 | 0.237 | 0.359 | 0.397 | 0.413 | 0.426 | 0.26 | 0.90 | 1.29 | 1.50 | 1.71 |
| | 1.75 | 1.00 | 0.309 | 0.399 | 0.426 | 0.431 | 0.435 | 0.53 | 1.30 | 1.71 | 1.78 | 1.85 |
| | 1.75 | 1.25 | 0.356 | 0.425 | 0.438 | 0.439 | 0.441 | 0.88 | 1.68 | 1.89 | 1.91 | 1.94 |
| Black | 2.25 | 0.50 | 0.209 | 0.319 | 0.378 | 0.409 | 0.440 | 0.18 | 0.59 | 1.07 | 1.45 | 1.93 |
| | 2.25 | 0.75 | 0.278 | 0.391 | 0.427 | 0.445 | 0.455 | 0.38 | 1.21 | 1.71 | 2.01 | 2.22 |
| | 2.25 | 1.00 | 0.335 | 0.432 | 0.453 | 0.458 | 0.463 | 0.70 | 1.80 | 2.15 | 2.28 | 2.38 |
| | 2.25 | 1.25 | 0.372 | 0.447 | 0.459 | 0.468 | 0.467 | 1.02 | 2.03 | 2.29 | 2.49 | 2.48 |
| Gum | 1.25 | 1.25 | — | 0.351 | 0.363 | 0.369 | 0.370 | — | 0.83 | 0.99 | 0.99 | 0.99 |
| | 1.50 | 1.25 | — | 0.377 | 0.390 | 0.390 | 0.391 | — | 1.06 | 1.20 | 1.20 | 1.21 |
| | 1.75 | 1.25 | — | 0.390 | 0.405 | 0.406 | 0.405 | — | 1.20 | 1.39 | 1.40 | 1.38 |
| | 2.25 | 1.25 | — | 0.417 | 0.428 | 0.429 | 0.430 | — | 1.56 | 1.73 | 1.75 | 1.77 |

[1] Philprene 1500.
[2] Philblack E, 42 phr.
[3] Recipe A, Table II.
[4] Santocure.
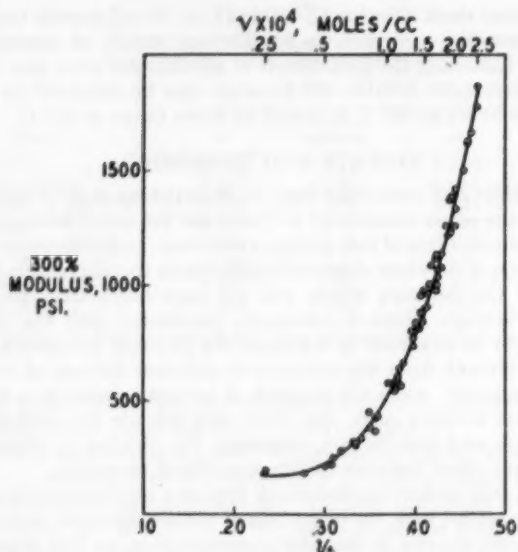
Fig. 1.—300% modulus versus density of network chains for cold SBR-SAF black stocks.

It is interesting to consider the magnitude of the apparent carbon black contribution to crosslinking and the rate at which it is developed during the cure (Table VII). The results indicate that the black contribution is proportional to the total number of network chains once the cure has leveled out and that, at least in the present example, it is developed at nearly the same rate as
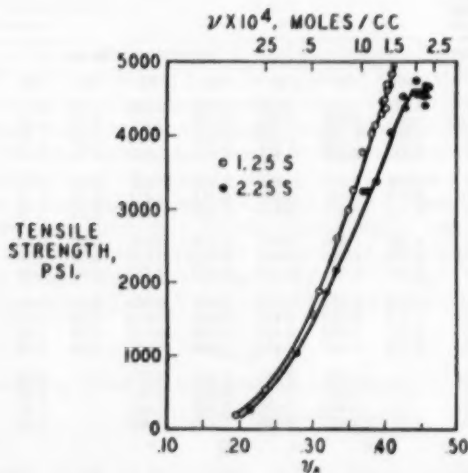


Fig. 2.—Tensile strength versus density of network chains for cold SBR-SAF black stocks.
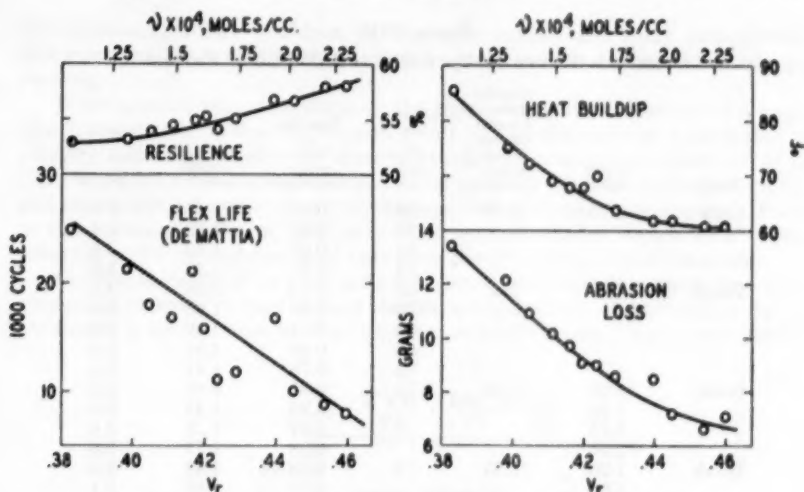
Fig. 3.—Dependence of resilience, flex life, heat buildup, and abrasion loss on density of network chains for cold SBR-SAF black stocks.

the vulcanization in absence of black. This, however, might not be the case with a slower accelerator.

Another point of interest is the apparent efficiency of the vulcanization reaction (Table VIII). Because of the filler contribution this efficiency will be about 40 per cent higher in the black stocks if equivalent amounts of sulfur have reacted. The results of free sulfur determinations show the expected trend. When black stocks are over-cured, some sulfur is split out, but no loss in apparent crosslinking results. It also appears that the sulfur reacting in the early stages of vulcanization is utilized somewhat less efficiently.

The results of gum vulcanizates agree closely with those of Scott and Magat[14] who found a ratio of $[S]/\nu$ of approximately four. Since $\nu$ is related to the number of crosslinks $n$ by

$$\nu = 2n - \frac{2\rho}{M} \tag{6}$$

## TABLE VII

### APPARENT BLACK CONTRIBUTION IN COLD SBR[1]— SAF BLACK[2] STOCKS[3]

| Sulfur (phr) | N-cyclo-hexyl-2-benzo-thiazole sulfen-amide[4] (phr) | $\nu$ black/$\nu$ gum at indicated cure time, min. | | | |
|---|---|---|---|---|---|
| | | 20 | 30 | 45 | 75 |
| 1.25 | 1.25 | 1.36 | 1.37 | 1.41 | 1.41 |
| 1.50 | 1.25 | 1.30 | 1.33 | 1.38 | 1.38 |
| 1.75 | 1.25 | 1.40 | 1.36 | 1.36 | 1.41 |
| 2.25 | 1.25 | 1.30 | 1.32 | 1.42 | 1.41 |

[1] Philprene 1500.
[2] Philblack E.
[3] Recipe A, Table II.
[4] Santocure.

TABLE VIII

COMBINED SULFUR IN COLD SBR[1]—SAF BLACK[2] STOCKS[3]

| Stock | Sulfur (phr) | N-cyclo-hexyl-2-benzo-thiazole sulfen-amide[4] (phr) | Cure time, min. | Fraction of total sulfur combined[5] | $\nu \times 10^4$, moles/cc. | [8]/$\nu$[6] |
|---|---|---|---|---|---|---|
| Gum | 1.75 | 1.25 | 20 | 0.89 | 1.20 | 3.8 |
|  |  |  | 30 | 0.94 | 1.39 | 3.4 |
|  |  |  | 45 | 0.97 | 1.40 | 3.6 |
|  |  |  | 75 | 0.97 | 1.38 | 3.6 |
| Black | 1.75 | 1.25 | 10 | 0.73 | 0.88 | 4.3 |
|  |  |  | 20 | 0.83 | 1.68 | 2.5 |
|  |  |  | 30 | 0.91 | 1.89 | 2.5 |
|  |  |  | 45 | 0.89 | 1.91 | 2.4 |
|  |  |  | 75 | 0.78 | 1.94 | 2.1 |
| Gum | 1.25 | 1.25 | 75 | 0.95 | 0.99 | 3.5 |
|  | 1.50 |  |  | 0.95 | 1.21 | 3.4 |
|  | 1.75 |  |  | 0.97 | 1.38 | 3.6 |
|  | 2.25 |  |  | 0.98 | 1.77 | 3.6 |
| Black | 1.25 | 1.25 | 75 | 0.88 | 1.40 | 2.3 |
|  | 1.50 |  |  | 0.79 | 1.67 | 2.1 |
|  | 1.75 |  |  | 0.78 | 1.94 | 2.1 |
|  | 2.25 |  |  | 0.97 | 2.48 | 2.6 |

[1] Philprene 1500.
[2] Philblack E.
[3] Recipe A, Table II.
[4] Santocure.
[5] Calculated from free sulfur analyses, method of Oldham, Baker and Craytor[16].
[6] [8] = Combined sulfur in gram atoms per cc. of polymer.

where $\rho$ is the density, and $M$ is the primary molecular weight of the polymer, roughly seven to eight sulfur atoms are required for the formation of each cross-link (omitting the relatively small term $2\rho/M$ from consideration). This fact, however, does not mean that the crosslinkage itself contains that many sulfur atoms. Recent work indicates this number to be probably no larger than two[16].
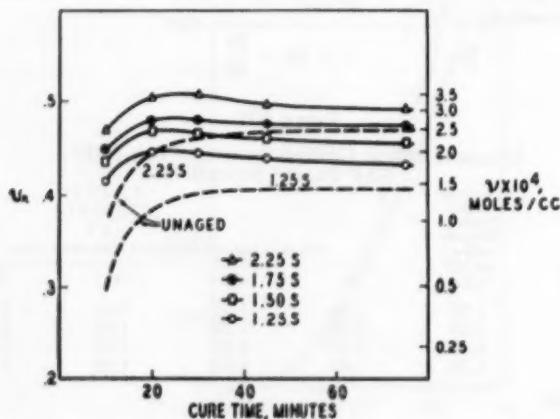


FIG. 4.—Effect of Geer oven aging on density of network chains for cold SBR-SAF black stocks (1.25 phr Santocure, sulfur as indicated).

The remaining sulfur combines to form zinc sulfide, and some undoubtedly forms intramolecular loops which are not counted in the determination of $\nu$ by swelling.

When scission effects accompany the processing or vulcanization of a polymer (breakdown, reversion), the end result will be the same as a reduction in primary molecular weight. If these effects are pronounced, the term $2\rho/M$ in Equation 6 may become appreciable. The quantity $\nu$ is then no longer unique, and significant differences in physical properties at equal $\nu$ may appear. Even in this instance, however, the number of network chains should be a better criterion of the overall degree of cure than the number of crosslinks alone.

*Increase in degree of cure on aging.*—Figure 4 illustrates the effect of accelerate daging on some of the stocks of the preceding section. The "unaged data" are shown in broken lines for the two extreme sulfur levels. Aging was carried
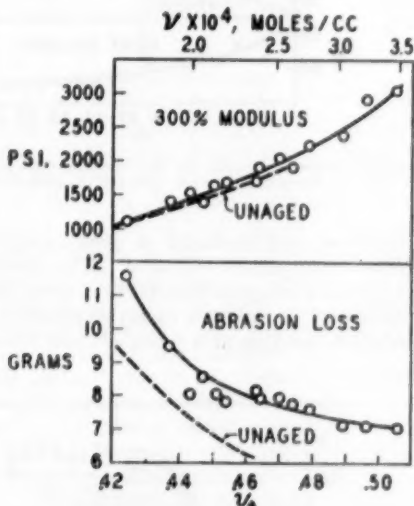


Fig. 5.—Effect of Geer oven aging on 300% modulus and abrasion loss as functions of the volume fraction of rubber in the swollen network; cold SBR-SAF black stocks.

out in a Geer oven for 24 hours at 212° F in air. It will be noted that the total crosslinking level after aging is in many instances higher for the shorter cure times than for the 75-minute cures. This effect is also reflected in the changes in physical properties of the stocks.

Figures 5 and 6 show the various physical test data as functions of $v_r$. Where the curves for the unaged stocks do not coincide with those for the aged data, the original curves have been dotted in for comparison. It appears that most of the changes in physical properties are due to additional crosslinking although tensile strength, modulus, resilience, and abrasion are affected somewhat differently than would be expected on the basis of further crosslinking alone. The slightly different relations between some of the physical properties and for unaged and aged vulcanizates can probably be accounted for by scission effects accompanying aging.
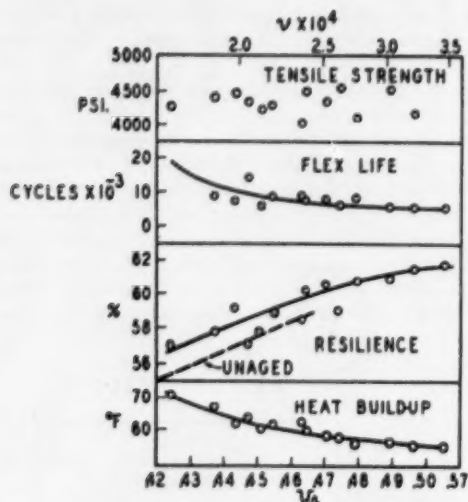
Fig. 6.—Effect of Geer oven aging on tensile strength, flex life, resilience, and heat buildup as functions of volume fraction of rubber in the swollen network; cold (41° F) SBR-SAF black stocks.

The changes in degree of cure produced on oven aging are due in part to postvulcanization effects and in part to oxidation.    The maximum in the curves for the aged stocks in Figure 4 suggests that there is some interaction between the two processes.    This may be due to a catalytic effect of small amounts of free sulfur on the oxidation reaction or a more efficient utilization of residual
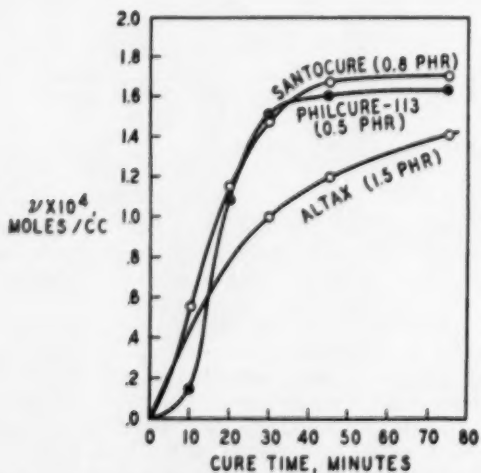


Fig. 7.—Cure rates for cold SBR-HAF black tread stocks with benzothiazyl disulfide (Altax), t-butyl-sulfenyl dimethyldithiocarbamate (Philcure 113), and N-cyclohexyl-2-benzothiazole-sulfenamide (Santo-cure) accelerators.

sulfur in the postvulcanization which, in the present example, was conducted at a much lower temperature.

*Acceleration.*—The swelling technique is ideally suited for the determination of rates of vulcanization as affected by the choice and the quantity of accelerator employed.    The data of Table VI show clearly that the ultimate degree of

TABLE IX

EFFECT OF EXTENDER OIL ON EFFECTIVE NUMBER OF NETWORK CHAINS[1]

| Mooney (ML-4) base polymer[2] | Black (phr) | Oil (phr) | $B_r$ | $\nu' \times 10^4$, moles/cc. | $\nu \times 10^4$, moles/cc. |
|---|---|---|---|---|---|
| 116 | 62.5 | 25 | 0.434 | 2.27 | 1.81 |
|  |  | 37.5 | 0.405 | 1.88 | 1.37 |
|  |  | 50 | 0.382 | 1.60 | 1.09 |
| 130 | 68.75 | 37.5 | 0.406 | 1.90 | 1.39 |
|  |  | 50 | 0.379 | 1.57 | 1.07 |
|  |  | 75 | 0.338 | 1.21 | 0.71 |

[1] Recipe D, Table II.
[2] Cold rubber (41° F styrene butadiene copolymer, SBR.)

vulcanization attained is dependent primarily on the sulfur level (almost a direct proportionality), with the Santocure accelerator determining mainly the rate of cure.

Rates with three different accelerators are shown in Figure 7 for cold rubber tread stocks containing 50 parts of HAF black.    The generally slow action of benzothiazyl disulfide (Altax), as well as the pronounced delayed action[17] of *t*-butyl-sulfenyl dimethyldithiocarbamate (Philcure 113) are clearly borne out.

*Oil-extended rubbers.*—The swelling method is readily adapted to measurements on oil-extended rubbers; it is only necessary to use Equation 2 or 3 to calculate the desired $\nu$.    It is found that the effect of the oil is to decrease the number of linkages per unit volume to an extent exceeding the dilution effect of the oil.    This can be seen clearly from a comparison of $\nu$ values (Table IX).

The decrease in the number of effective crosslinks in oil-extended stocks is probably due to a reduction in the efficiency of vulcanization.    The greater separation of the polymer chains coupled with their increased mobility should favor the formation of intramolecular crosslinks.    In addition, the possibility of a direct reaction of sulfur with the plasticizer cannot be discounted.

TABLE X

CROSSLINKING OF OIL–EXTENDED POLYMERS CONTAINING 50 PARTS HAF BLACK

| Base polymer Mooney (ML-4) | Oil level (phr) | Oil masterbatch Mooney (ML-4) | $\nu/\nu_0$ |
|---|---|---|---|
| 52 | 0 | 52 | 1.44 |
| 116 | 25 | 61 | 1.36 |
| 130 | 37.5 | 57 | 1.31 |
| 150 | 50 | 41 | 1.31 |

Another point of interest is the apparent carbon black contribution to crosslinking.    Data in Table X were obtained at the usual loading of black, i.e., 50 parts HAF black per 100 parts of extended polymer.

The value of $\nu_0$ is for the oil-extended gum stock.    The results indicate a slight reduction in the relative carbon black contribution at increasing oil levels.

*Carbon black type and loading.*—A number of investigators have attempted to explain the contribution of fillers to the total degree of crosslinking in terms of filler to rubber linkages of adsorptive nature. The most rigorous treatment of this sort is that of A. M. Bueche[9], whose theory leads to the following expression for the quantity $\nu$ (in the notation of this paper—not exactly equivalent to Bueche's notation)

$$\nu = 2n - \frac{2\rho}{M} + \frac{3f}{N_a r} \cdot \frac{v_2}{1 - v_2} (1 + F) \tag{7}$$

where $f$ *is the number of filler attachments per unit area of filler surface*, $N_a$ *is Avogadro's number*, $r$ *is the mean radius of the filler particle and* $v_2$ *is the volume fraction of filler in the vulcanizate* with $n$, $\rho$, and $M$ as defined in Equation 6. The quantity $F$ is equal to

$$F = 1 + \frac{\rho}{M_e} \left( N_a \epsilon - \frac{1}{n} \right) \tag{8}$$

where $M_e$ *is the molecular weight of a molecular loop formed by adsorption of the filler*, and $\epsilon$ *is the volume of a single structure capable of crosslinkage*. It must be understood that in order for an adsorptive linkage to be counted in a swelling test, it must resist desorption by the solvent; its origin must therefore be chemisorption or at least physical adsorption at active centers.

If the filler were to contribute adsorptive crosslinkages independently of the vulcanization reaction, $\nu$ might be expected to vary linearly with $v_2/(1 - v_2)$. In addition the slope of the straight lines should be inversely proportional to particle size (i.e., essentially proportional to specific surface area) for carbon blacks of similar specific adsorptive capacity ($f$).

Data of Table XI in which eight blacks of widely different surface area are compared at four different loadings show that this is far from being the case. It is found that the number of apparent strong linkages contributed by the filler is not generally dependent on surface area—an observation in agreement with the findings of Blanchard and Parkinson[18] who derived their results from modulus determinations on prestretched rubbers. To identify the "filler contributed" linkages with actual "filler-to-rubber linkages" one would have to postulate that $f$ decreases progressively as the particle size decreases. This is certainly unreasonable for a series of similar carbons such as the furnace blacks (FEF, HAF, and SAF), and independent evidence from adsorption experiments of elastomers on carbon blacks[13] does not give any indication of such a trend.

There are two possible explanations for the observed behavior. One might surmise that large surface area blacks adsorb appreciable amounts of curatives, thus decreasing $n$ and canceling some of the effect of the adsorptive linkages. Although small quantities of free sulfur have been detected in SAF black stocks (Table VIII), this is not believed to occur to any large extent for the reason that the loss in intermolecular sulfur linkages would have to be very large to explain, for instance, the behavior of SAF black relative to SRF black with only one-fifth the surface area. It would mean that the number of adsorptive linkages in SAF black stocks might have to be as high as $10^{-4}$ moles/cc. or more, in which case it would be difficult to see why sulfur is required at all to produce a reasonably tightly cured network in an SAF black stock. Determination of $\nu$ on black-rubber masterbatches heated to normal vulcanization temperatures indicate the number of linkages[13] produced in the absence of sulfur to be very

TABLE XI

EFFECT OF CARBON BLACK TYPE AND LOADING ON EFFECTIVE CROSSLINKING OF COLD RUBBER STOCKS[1]

| Type | Black name | Surface area, sq. m./g. | Loading, phr | $\nu$ | $\nu \times 10^4$, moles/cc. | 300% modulus, psi | Tensile, psi | Elongation, % | Resilience, % | ΔT °F | Abrasion loss, cc. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| FT | None | 17 | — | 0.388 | 1.18 | 180 | 210 | 360 | 79.0 | 31.5 | 137 |
|  | P-33 |  | 12.5 | 0.389 | 1.19 | 220 | 570 | 560 | 78.1 | 34.4 | 76.8 |
|  |  |  | 25 | 0.390 | 1.20 | 280 | 550 | 450 | 76.3 | 36.5 | 56.8 |
|  |  |  | 37.5 | 0.397 | 1.28 | 390 | 2000 | 800 | 73.3 | 40.5 | 49.3 |
|  |  |  | 50 | 0.399 | 1.31 | 500 | 2200 | 750 | 72.6 | 47.3 | 38.2 |
| SRF | Gastex | 35 | 12.5 | 0.394 | 1.25 | 310 | 1300 | 600 | 76.9 | 36.1 | 51.1 |
|  |  |  | 25 | 0.402 | 1.34 | 530 | 1830 | 600 | 74.7 | 41.2 | 23.2 |
|  |  |  | 37.5 | 0.406 | 1.41 | 890 | 2480 | 580 | 72.6 | 49.7 | 19.7 |
|  |  |  | 50 | 0.413 | 1.50 | 1250 | 2750 | 550 | 70.6 | 54.1 | 17.4 |
| FEF | Philblack A | 65 | 12.5 | 0.393 | 1.23 | 350 | 1040 | 510 | 77.2 | 36.8 | 38.7 |
|  |  |  | 25 | 0.404 | 1.38 | 750 | 2730 | 620 | 74.3 | 45.9 | 19.7 |
|  |  |  | 37.5 | 0.417 | 1.56 | 1375 | 3150 | 530 | 71.1 | 50.7 | 13.1 |
|  |  |  | 50 | 0.425 | 1.69 | 2100 | 3240 | 460 | 68.7 | 61.2 | 9.2 |
| HAF | Philblack O | 94 | 12.5 | 0.392 | 1.22 | 530 | 1520 | 470 | 76.5 | 37.5 | 30.6 |
|  |  |  | 25 | 0.402 | 1.34 | 740 | 3040 | 600 | 73.1 | 45.6 | 14.5 |
|  |  |  | 37.5 | 0.412 | 1.49 | 1430 | 3800 | 540 | 69.3 | 55.1 | 9.0 |
|  |  |  | 50 | 0.417 | 1.56 | 2100 | 3690 | 450 | 64.2 | 63.2 | 5.2 |
| SAF | Philblack E | 138 | 12.5 | 0.390 | 1.20 | 360 | 1700 | 600 | 74.0 | 39.9 | 30.5 |
|  |  |  | 25 | 0.400 | 1.32 | 680 | 3930 | 670 | 69.2 | 49.0 | 10.5 |
|  |  |  | 37.5 | 0.415 | 1.54 | 1160 | 4000 | 600 | 64.6 | 59.1 | 5.8 |
|  |  |  | 50 | 0.430 | 1.76 | 1880 | 4160 | 500 | 57.2 | 72.6 | 3.2 |
| — | Acetylene | 58 | 12.5 | 0.401 | 1.33 | 400 | 960 | 500 | 73.5 | 41.5 | 41.7 |
|  |  |  | 25 | 0.415 | 1.53 | 830 | 2200 | 565 | 70.0 | 50.0 | 21.4 |
|  |  |  | 37.5 | 0.421 | 1.62 | 1440 | 3090 | 575 | 67.4 | 63.5 | 13.1 |
|  |  |  | 50 | 0.440 | 1.92 | 2180 | 3280 | 460 | 61.9 | 76.0 | 9.4 |
| EPC | Wyex | 89 | 12.5 | 0.398 | 1.30 | 300 | 1570 | 620 | 73.7 | 40.5 | 38.2 |
|  |  |  | 25 | 0.411 | 1.47 | 550 | 3320 | 690 | 69.6 | 49.3 | 19.2 |
|  |  |  | 37.5 | 0.417 | 1.56 | 940 | 4020 | 660 | 64.5 | 59.1 | 11.9 |
|  |  |  | 50 | 0.424 | 1.67 | 1380 | 3980 | 610 | 59.7 | 70.9 | 7.8 |
| Graphitized Channel | Graphon | 113 | 12.5 | 0.389 | 1.19 | 210 | 660 | 635 | — | — | 38.0 |
|  |  |  | 25 | 0.391 | 1.22 | 240 | 1890 | 750 | — | — | 31.6 |
|  |  |  | 37.5 | 0.392 | 1.23 | 250 | 2940 | 770 | — | — | 16.1 |
|  |  |  | 50 | 0.396 | 1.27 | 290 | 2840 | 750 | — | — | 12.6 |

[1] Recipe E; cured 45 minutes at 307° F.

much smaller, of the order of $10^{-5}$ moles/cc. Nuclear magnetic resonance experiments also fail to give any evidence for a large number of strong polymer to filler bonds[19].

The correct explanation is believed to be the following. The apparent contribution of a filler to crosslinking is composed of three components: (a) actual filler to rubber linkages which are relatively small in number and, while proportional to surface area, are masked by the other two effects which are (b) filler-induced intermolecular linkages and (c) an effect of particle shape or "structure". In this picture reinforcement is still thought to be influenced profoundly by the effects of adsorptive linkages, but ν becomes representative mainly of the intermolecular crosslinks.

Recent evidence[20-22] suggests that carbon black-to-rubber linkages are formed by interaction of polymeric free radicals with the black either during milling or in vulcanization. In the latter case it would be conceivable that the entire contribution of the filler might constitute black-to-polymer linkages were it not
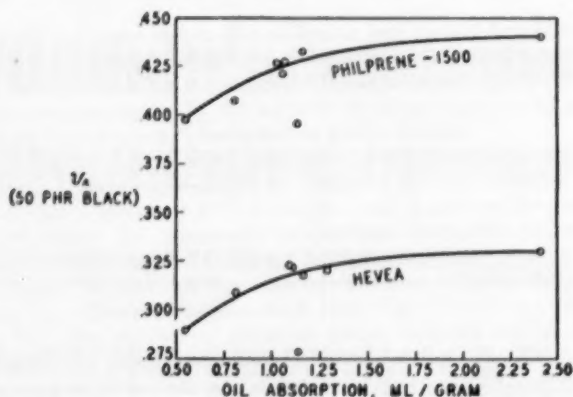


Fig. 8.—Relation between degree of swelling and carbon black structure, as measured by oil absorption for cold SBR and natural rubber stocks containing 50 phr of blacks of various types.

again for the peculiar apparent reduction in surface density of adsorption points for carbon blacks of small particle size. It seems almost certain that in a complex filler-modified vulcanization reaction the two types of linkages would not be formed independently of each other so that only a part of the increase in crosslinking need be due to actual points of attachment on the filler surface.

It should also be recalled that a certain number of adsorptive linkages will become effective only on development of the network as indicated by Bueche's theory (Equation 8). This effect, however, could hardly account for the almost direct proportionality of the apparent black contribution to overall level of cure (Table VII). However, an increase in the number of intermolecular crosslinks because of interaction of the vulcanization reaction with the carbon black could easily produce such a relation. One would not expect this effect to be independent of the curing system so that the "black contribution" will vary for various types of vulcanization. This is shown to be the case in a section of this discussion devoted to special vulcanization systems.

The connection with particle or aggregate shape is illustrated in Figure 8

## TABLE XII

### CROSSLINKING IN SILICA-LOADED COLD RUBBER[1]

| Hydrated silica[2], phr | Sulfur, phr | N-cyclo-hexyl-2-benzo-thiazole sulfen-amide[3], phr | Cure time, min. | 300% modulus, psi | Tensile, psi | Elon-gation, % | Shore hardness | NBS abrasion, rev./mil. | ν | ν ×10³, moles/cc. |
|---|---|---|---|---|---|---|---|---|---|---|
| 50 | 1.75 | 1.5 | 15 | 370 | 2280 | 1110 | 55 | 2.60 | 0.365 | 0.95 |
|  |  |  | 30 | 390 | 2620 | 1130 |  |  | 0.392 | 1.23 |
|  |  |  | 45 | 370 | 2600 | 1150 |  |  | 0.394 | 1.25 |
| — | 1.75 | 1.5 | 15 | 230 | 300 | 400 |  |  | 0.428 | 1.73 |
|  |  |  | 30 | 220 | 340 | 430 |  |  | 0.426 | 1.70 |
|  |  |  | 45 | 230 | 330 | 440 |  |  | 0.434 | 1.83 |
| 50 | 1.75 | 3 | 15 | 620 | 3260 | 950 | 60 | 2.60 | 0.433 | 1.81 |
|  |  |  | 30 | 590 | 2600 | 890 |  |  | 0.436 | 1.85 |
|  |  |  | 45 | 560 | 2700 | 940 |  |  | 0.433 | 1.81 |
| — | 1.75 | 3 | 15 | 290 | 300 | 320 |  |  | 0.442 | 1.96 |
|  |  |  | 30 | 280 | 360 | 370 |  |  | 0.448 | 2.09 |
|  |  |  | 45 | 270 | 320 | 350 |  |  | 0.447 | 2.06 |
| 50 | 3.5 | 1.5 | 15 | 610 | 2660 | 870 | 64 | 2.45 | 0.450 | 2.11 |
|  |  |  | 30 | 690 | 2800 | 820 |  |  | 0.481 | 2.82 |
|  |  |  | 45 | 700 | 2800 | 820 |  |  | 0.488 | 2.98 |
| — | 3.5 | 1.5 | 15 | — | 390 | 270 |  |  | 0.469 | 2.53 |
|  |  |  | 30 | — | 340 | 270 |  |  | 0.478 | 2.75 |
|  |  |  | 45 | 360 | 460 | 360 |  |  | 0.487 | 2.97 |
| 50 | 3.5 | 3 | 15 | 910 | 1990 | 550 | 66 | 2.20 | 0.494 | 3.15 |
|  |  |  | 30 | 880 | 2440 | 640 |  |  | 0.499 | 3.29 |
|  |  |  | 45 | 840 | 2350 | 650 |  |  | 0.503 | 3.41 |
| — | 3.5 | 3 | 15 | — | 360 | 230 |  |  | 0.489 | 3.02 |
|  |  |  | 30 | — | 340 | 230 |  |  | 0.496 | 3.21 |
|  |  |  | 45 | — | 370 | 250 |  |  | 0.496 | 3.21 |

[1] Recipe H, Table II; cure temperature, 307° F.
[2] Hi-Sil 101.
[3] Santocure.

where swelling data are plotted against oil absorption. As "structure" is not the only factor involved, the correlation is not perfect; for instance, it fails completely for the devolatilized channel black, Graphon. It has been found to fail also for butyl rubber (Table XIV).

Some effect of structure on inhibition of swelling is to be expected intuitively. One need only visualize a row of spherical particles fused into a chain as compared to the same particles separated from each other. Everything else being the same, the connecting links will impart a measure of rigidity to the structure which should manifest itself in increased resistance to swelling of the matrix in which the particles are embedded.

*Silica-loaded stocks.*—It is commonly known that silica and the other mineral pigments differ characteristically from carbon black in their effect on the apparent degree of vulcanization of elastomers. Since the swelling method for the determination of crosslinking explains many of the properties of black-loaded stocks, this technique was applied to a typical mineral filler stock. The pigment chosen was Hi-Sil 101 a silica of the following physical properties:

| | |
|---|---|
| Mean particle diameter | 300°Å |
| BET surface area | 110 sq. m./g. |
| pH | 8.5 to 9.0 |
| Density | 2.18 g./cc. |

Comparison of the values of $\nu$ for the white and gum stocks (Table XII) shows that Hi-Sil 101 produces no significant increase in overall crosslinking level. On the contrary, while 3.5 phr of sulfur in the white stocks lead to vulcanizates of total degree of cure approximately equal to that of the gum controls, there is a pronounced decrease in $\nu$ at the lower sulfur level. At the same time the rate of cure does not appear to be influenced too strongly by the silica, particularly at the higher accelerator level. Free sulfur determinations (45-minute cure) in Table XIII showed no significant differences in the amount of unreacted sulfur in white and gum stocks.

The large effect of doubling the accelerator level in the white stocks on the ratio $[S]/\nu$, as contrasted to the lesser effect observed in the gum stocks, suggests that inactivation of accelerator by the silica may be the decisive factor in decreasing the efficiency of the vulcanization reaction at low to moderate sulfur levels.

The trends in the physical properties of the white stocks with degree of vulcanization exhibit some departures from the behavior commonly observed in

TABLE XIII

FREE SULFUR IN WHITE AND GUM STOCKS

| Sulfur, phr | N-cyclo-hexyl 2-benzo-thiazole sulfen-amide[1], phr | % Free sulfur[2] | | $[S]^{2}/\nu$ | |
|---|---|---|---|---|---|
| | | White | Gum | White | Gum |
| 1.75 | 1.5 | 0.05 | 0.04 | 3.9 | 2.7 |
| 1.75 | 3.0 | 0.05 | 0.07 | 2.7 | 2.4 |
| 3.5 | 1.5 | 0.02 | 0.03 | 2.9 | 2.9 |
| 3.5 | 3.0 | 0.05 | 0.06 | 2.5 | 2.7 |

[1] Santocure.
[2] Method of reference[16].
[3] $[S]$ = Combined sulfur in gram atoms per cc of polymer.

## TABLE XIV

### EFFECT OF CARBON BLACK TYPE ON THE NUMBER OF NETWORK CHAINS IN HEVEA AND BUTYL STOCKS[1]

| Type | Black name | Oil absorption cc./g. | Hevea | | | Butyl | | |
|------|------------|------------|------|------|------|------|------|------|
| | | | $v_r$ | $v \times 10^4$, moles/cc. | $v/v_0$ | $v_r$ | $v \times 10^4$, moles/cc. | $v/v$ |
| — | — | — | 0.271 | 0.93 | 1.00 | 0.282 | 0.85 | 1.00 |
| FT | P-33 | 0.56 | 0.290 | 1.12 | 1.22 | 0.303 | 1.06 | 1.25 |
| SRF | Gastex | 0.81 | 0.308 | 1.35 | 1.45 | 0.334 | 1.42 | 1.67 |
| FEF | Philblack A | 1.17 | 0.319 | 1.50 | 1.61 | 0.338 | 1.47 | 1.73 |
| HAF | Philblack O | 1.14 | 0.322 | 1.54 | 1.66 | 0.340 | 1.50 | 1.77 |
| SAF | Philblack E | 1.28 | 0.322 | 1.54 | 1.66 | 0.325 | 1.30 | 1.53 |
| — | Acetylene | 2.40 | 0.330 | 1.65 | 1.78 | 0.326 | 1.32 | 1.55 |
| EPC | Wyex | 1.13 | 0.323 | 1.56 | 1.68 | 0.303 | 1.06 | 1.25 |
| C | Graphon | 1.13 | 0.277 | 0.98 | 1.06 | 0.284 | 0.86 | 1.01 |

[1] Recipes F, G, Table II; 50 phr of indicated black, cured 45 minutes at 307° F.

carbon black-reinforced stocks.    Tensile and abrasion resistance are surprisingly insensitive to changes in $v$; on the other hand, modulus, elongation, and Shore hardness display the expected variations with degree of crosslinking (Table XII).

*Hevea and butyl rubbers.*—The considerations presented for styrene/butadiene copolymers apply equally to other hydrocarbon elastomers.    Table XIV shows the results with various carbon blacks (at 50 phr) for Hevea and butyl rubbers.    The only difference from the behavior of cold SBR rubber is the apparent failure of the correlation of vulcanizate swelling, with carbon black-oil absorption for butyl rubber.    The trends of physical properties with $v$ at variable curative levels (not shown) are similar as for SBR.    The typical reversion of Hevea stocks on overcure is always reflected in a drop in $v$.

In principle the swelling method allows an absolute comparison of the degree of vulcanization of chemically different polymers if the correct solubility parameter $\mu$ is used in calculating $v$ from $v_r$.    It is interesting, therefore, to compare cold SBR rubber with natural rubber and butyl at equal number of network chains (Table XV).    A similar balance of physical properties is obtained in each case.

Another interesting comparison is afforded by the data on butyl gum vulcanizates.    Zapp and associates[15] reported values of $M_c$ (equal to $\rho/v$) for butyl stocks in almost the identical recipe used here and under similar vulcanization conditions.    The agreement (Table XVI), though possibly fortuitous, is nevertheless remarkable.

## TABLE XV

### PROPERTIES OF VULCANIZATES AT EQUAL $v$
### $v = 1.65 \times 10^{-4}$ moles/cc.
### Reinforcement: 50 phr HAF Black[1]

| Rubber | Recipe | Cure time, min. | 300% modulus, psi | Tensile, psi | Elongation, % | Shore hardness |
|--------|--------|------|------|------|------|------|
| Cold SBR[2] | E | 45 | 2180 | 3740 | 425 | 62 |
| No. 1 RSS | F | 20 | 2180 | 3900 | 470 | 58 |
| Butyl[3] | G | 75 | 1910 | 2420 | 395 | 65 |

[1] Philblack O.
[2] Philprene 1500.
[3] Enjay Butyl 217.

## TABLE XVI

### CORRELATION OF DATA ON BUTYL GUM VULCANIZATES

| Author | Cure temperature, °F | Cure time, minutes | $\nu \times 10^4$, moles/cc. |
|---|---|---|---|
| Zapp et al. | 300 | 10 | 0.57 |
| | | 20 | 0.85 |
| | | 40 | 0.98 |
| | | 80 | 1.01 |
| This work | 307 | 10 | 0.47 |
| | | 30 | 0.85 |
| | | 45 | 0.94 |
| | | 75 | 1.01 |

*Special vulcanization systems.*—Table XVII shows some data on cold SBR (Philprene 1500) vulcanized with dicumyl peroxide both in the absence and presence of HAF black. The results leave little doubt that the carbon black exerts a repressing effect on the cure although there is no apparent retardation of the cure rate.

In sulfur-cured stocks the incorporation of 50 phr of HAF black (Philblack 0) results in a 40% increase in effective crosslinking. In the peroxide cure the

## TABLE XVII

### CROSSLINKING IN PEROXIDE–CURED COLD SBR[1]

| Dicumyl peroxide[3], phr | Cure time, min. | 300% modulus, psi | Tensile, psi | Elongation, % | $\nu_r$ | $\nu \times 10^4$ moles/cc. | % Extractable |
|---|---|---|---|---|---|---|---|
| | | | Gum Stocks | | | | |
| 0.5 | 15 | 80 | 440 | 1210 | 0.183 | 0.13 | 24.2 |
| | 30 | 180 | 460 | 1200 | 0.218 | 0.19 | 18.3 |
| | 45 | 110 | 560 | 1140 | 0.222 | 0.20 | 18.3 |
| | 75 | 100 | 490 | 1140 | 0.230 | 0.22 | 18.0 |
| 1.0 | 15 | 190 | 280 | 440 | 0.295 | 0.47 | 13.1 |
| | 30 | 280 | 310 | 340 | 0.336 | 0.71 | 10.1 |
| | 45 | 220 | 340 | 450 | 0.337 | 0.71 | 9.9 |
| | 75 | 220 | 240 | 330 | 0.335 | 0.70 | 9.9 |
| 2.0 | 15 | — | 200 | 240 | 0.346 | 0.78 | 9.3 |
| | 30 | — | 200 | 160 | 0.400 | 1.32 | 6.9 |
| | 45 | — | 210 | 160 | 0.398 | 1.29 | 6.8 |
| | 75 | — | 80 | 30 | 0.399 | 1.30 | 7.0 |
| | | | Black Stocks (50 phr HAF Black[2]) | | | | |
| 0.5 | 15 | 260 | 510 | 750 | 0.210 | 0.18 | 28.4 |
| | 30 | 300 | 610 | 700 | 0.215 | 0.19 | 26.8 |
| | 45 | 340 | 720 | 740 | 0.224 | 0.21 | 26.1 |
| | 75 | 360 | 800 | 710 | 0.239 | 0.25 | 24.9 |
| 1.0 | 15 | 730 | 2060 | 660 | 0.299 | 0.48 | 15.3 |
| | 30 | 780 | 2190 | 650 | 0.308 | 0.53 | 14.3 |
| | 45 | 820 | 2170 | 625 | 0.309 | 0.54 | 14.3 |
| | 75 | 840 | 2320 | 640 | 0.312 | 0.55 | 14.4 |
| 2.0 | 15 | 2330 | 2840 | 350 | 0.417 | 1.56 | 8.0 |
| | 30 | 2440 | 2990 | 350 | 0.418 | 1.59 | 7.8 |
| | 45 | 2400 | 3250 | 370 | 0.417 | 1.57 | 8.3 |
| | 75 | 2390 | 3300 | 380 | 0.419 | 1.59 | 7.8 |

[1] Recipe I; cure temperature, 307° F.
[2] Philblack O.
[3] Di-Cup (Hercules Powder Co., Wilmington, Del.).

maximum apparent "black contribution" is about 20% at the two-phr level. At the one-phr level the gum stock is actually cured more tightly than the black stock.

At all peroxide contents the black stocks contain more extractable matter. The results are a good illustration of how apparent changes in degree of cross-linking brought about by incorporation of fillers are themselves dependent on the vulcanization system.

Figure 9 illustrates the effect of gamma irradiation on SBR-HAF black (Philprene 1500-Philblack 0) masterbatch. The data, though scattered, are sufficient to establish roughly the expected proportionality between degree of cure and radiation dosage.

Another interesting vulcanization reaction is the cure of butadiene-2-methyl-5-vinylpyridine copolymers with organic halides.  Table XVIII shows results
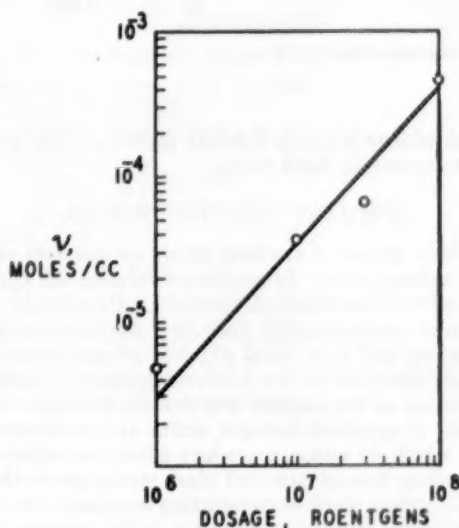


FIG. 9.—Degree of vulcanization versus gamma radiation dosage for cold SBR-HAF black stock.

of the cure of such a polymer with benzotrichloride as well as in a conventional sulfur recipe.

When the copolymer is cured with a quaternizing agent, the resulting polar groups decrease the solubility very strongly; in fact, the quaternized polymers are excellent oil-resistant rubbers[6,23]. For this reason the swelling determinations were run in benzene, a better solvent than $n$-heptane.  The solubility parameter for the quaternized gum extrapolates to $\mu = 0.42$ at infinite dilution (Table I) which is nearly the same as for the conventional stock.  This is, of course, not unusual as the degree of vulcanization depends on the benzotrichloride content so that the point of no cure ($v_r = 0$) corresponds to a stock free of curatives.

The contribution of the SAF black to crosslinking is again found to be dependent on the curing system.  The results also show that good oil resistance

## Table XVIII

BUTADIENE–2–METHYL–5–VINYLPRIDINE[1] CURED CONVENTIONALLY AND WITH BENZOTRICHLORIDE[2]

| SAF black[3], phr | Curing system | Cure time, minutes | $v_r$[4] | $v \times 10^4$, moles/cc. |
|---|---|---|---|---|
| — | Benzotrichloride | 20 | 0.228 | 0.58 |
| | | 30 | 0.235 | 0.61 |
| | | 45 | 0.248 | 0.66 |
| 50 | Benzotrichloride | 20 | 0.312 | 1.01 |
| | | 30 | 0.312 | 1.01 |
| | | 45 | 0.317 | 1.04 |
| — | Sulfur | 20 | 0.147 | 0.73 |
| | | 30 | 0.152 | 0.75 |
| | | 45 | 0.154 | 0.78 |
| 50 | Sulfur | 20 | 0.213 | 1.61 |
| | | 30 | 0.217 | 1.67 |
| | | 45 | 0.221 | 1.76 |

[1] Philprene VP-25.
[2] Recipes K and L; cure temperature, 307° F.
[3] Philblack E.
[4] In benzene.

of the quaternized rubbers is due to the high polarity of the quaternary groupings rather than to unusually tight cures.

## SUMMARY AND CONCLUSIONS

The Flory-Rehner theory of swelling allows an estimate of the number of crosslinks in gum vulcanizates. In reinforced rubbers the apparent degree of crosslinking is raised by some fillers, particularly carbon blacks.

It has been shown experimentally that, for vulcanizates of a given polymer at a fixed filler loading and type, most physical properties are, in the first approximation, simple functions of the apparent number of network chains per unit volume, regardless of the possible origin of the linkages. Aside from controlling the number of apparent linkages, sulfur and accelerator levels as well as cure time have relatively minor, secondary effects on vulcanizate properties. Comparison of swelling data of gum and black stocks shows that the apparent contribution of the carbon black to crosslinking increases with the level of cure. Softeners and extender oils cause a reduction in the number of linkages, presumably by reducing the efficiency of sulfur utilization.

It has been demonstrated that the swelling of vulcanizates in solvents gives an accurate measure of the degree of vulcanization even in filler-reinforced stocks. The results are apparently not obscured by adsorptive linkages between filler and polymer. When chemically different polymers are compared, the swelling volumes may be used to calculate the density of effective network chains; thus a nearly absolute measure of the degree of vulcanization is obtained.

The swelling method is not difficult to apply, requires no special equipment, and imposes no limitation on the size or shape of the test specimen. For instance, it has been used with excellent success in this laboratory to check the state of cure in test-fleet tires. A small sample is cut from the side of the first rib of a tire and tested in the usual manner.

The data presented offer some insight into the question of reinforcement. The evidence points to the fact that "contributions" of fillers to crosslinking derived from subtraction of the number of network chains or crosslinks in the filled and gum vulcanizates do not quantitatively represent the number of

filler-to-rubber linkages.   This filler "contribution" depends on the degree of cure, the vulcanization system, and the filler particle or aggregate shape.   It depends only slightly on the particle size or surface area of the filler.   The most plausible explanation of the observed behavior lies in a superposition of the effects of the filler on the course of vulcanization, filler-to-rubber linkages, and particle shape or aggregate structure.

## ACKNOWLEDGMENT

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# A STUDY OF VULCANIZATION ACCELERATORS. I. COMPOUNDS WHICH REACT ANALOGOUSLY TO RUBBER *

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## INTRODUCTION

In the field of rubber vulcanization, the reactions of sulfur with methyl-butene[1,2] or with cyclohexene[3], which possess isoprenic structures, have already been fully investigated. These model substances, however, seem to have some disadvantages because of difficulty in obtaining them and relatively low boiling points which lead to carrying out the model reactions in sealed tubes.

The present investigation reports the effect of several accelerators upon reactions between sulfur and various model compounds, which do not necessarily involve the isoprenic structure, but which may be expected to reveal reactivities similar to that of rubber. All the model compounds examined here have boiling points higher than the ordinary vulcanization temperature.

Although not a few problems are still obscure in regard to the mechanism of vulcanization[4], it may be possible, with reference to the available experimental results, to interpret vulcanization in terms of the following two mechanisms:

A. Attack of sulfur on the $\alpha$-methylene group.
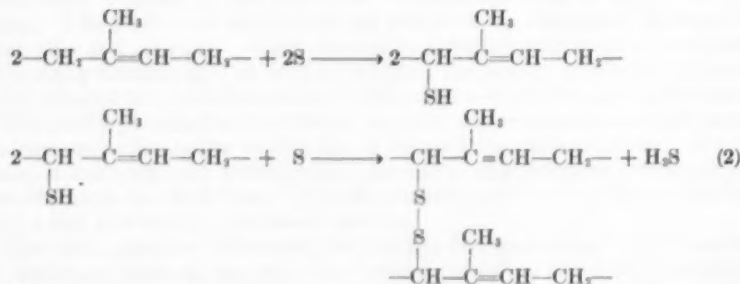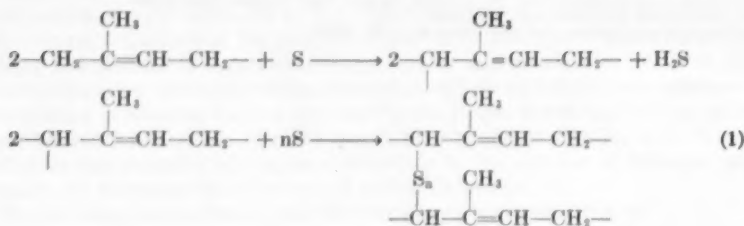
B. Addition of sulfur to the double bond.

$$2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=CH-CH_2- + 2S \longrightarrow 2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle S}{|}}{C}}-CH-CH_2- \qquad (3)$$

$$2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle SH}{|}}{C}}=C-CH_2- \xrightarrow{+S} -CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle S}{|}}{C}}=C-CH_2-+H_2S \qquad$$

$$2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle S}{\diagup\diagdown}}{C}}-CH-CH_2-$$

$$\overset{|}{S}$$

$$-CH_2-\overset{\overset{\textstyle CH_3}{|}}{C}=C-CH- \qquad (4)$$

$$2-CH_2-\overset{\overset{\textstyle CH_3}{|}}{CH}-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle S}{|}}{C}}-CH_2- \longrightarrow CH_2-\overset{\overset{\textstyle CH_3}{|}}{CH}-\overset{}{C}-CH_2-$$

$$-CH_2-\overset{}{CH}-\overset{}{C}-CH_2- \qquad (5)$$
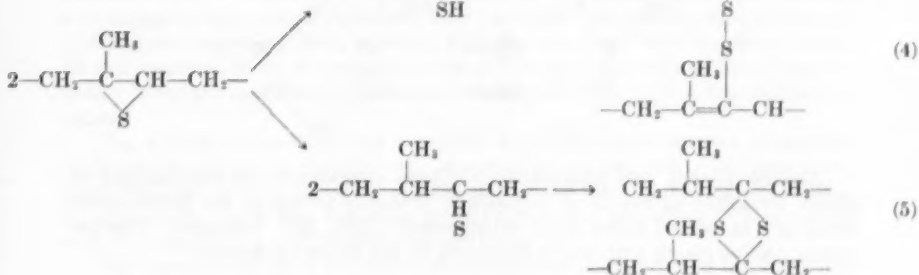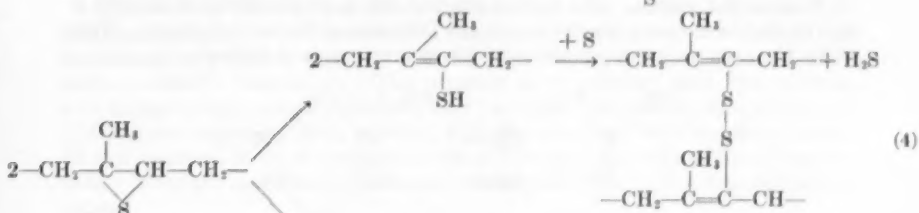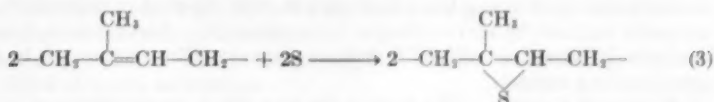
From the reaction scheme indicated above, in the case of intermolecular crosslinking, it is seen that hydrogen sulfide is not evolved only in Reaction (5), the formation of polythioketone-type bond[5]. On the other hand, Armstrong[2] and his collaborators found the modulus of vulcanized rubber to be proportional to the amount of zinc sulfide rather than to that of combined sulfur. Gee[6] and Hull[7] also reported that the number of crosslinkages in vulcanized rubber could be determined by analyzing for zinc sulfide.

The purpose of vulcanizing rubber is considered to be the formation of crosslinks between rubber molecules. In the industrial process of vulcanization using accelerators, it may reasonably be expected also that crosslink formation proceeds parallel to the evolution of hydrogen sulfide, i.e., to the dehydrogenation reaction of rubber.

In the sense described above, the present writers followed the reactions between sulfur and model compounds by analyzing for hydrogen sulfide or zinc sulfide.

These reactions seem to be so closely correlated with rubber vulcanization that they may serve as an aid to studies of the mechanism of vulcanization. Furthermore, they will be successfully applied in industry as an easier testing method for accelerators, since all of the model substances used here are quite familiar and have relatively high boiling points.

### MODEL COMPOUNDS

*Tetralin.*—In comparing the molecular structures, it can be considered that the carbon atom at the 1- or 4-position of tetralin will correspond to that at the α-position of the isoprenic unit in rubber.
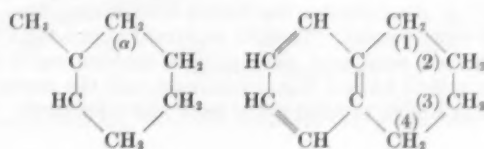
For example, the hydrogen atom at the 1-position of tetralin is readily removed in the same way as the α-hydrogen atom of the rubber molecule[8,9]. They are easily oxidized by air resulting in hydroperoxide. Furthermore, it is known that tetralin as well as rubber[10,11] reduces aromatic nitro compounds to give the corresponding amines.

*Toluene and xylene.*—The carbon atom at the o- or p-position of toluene is slightly rich in electron density due to the influence of the methyl group. This is also the case with the γ-position of the isoprenic unit in rubber.
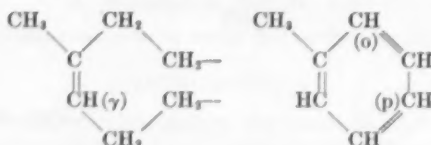


*Aniline, phenol, and phenylhalide.*—These compounds are also subject to attack by sulfur at the o- or p-position, probably owing to the electromeric effect of the benzyl anion type substituents ($NH_2$, $OH$, halogen). For example, aniline reacts with sulfur according to the following scheme:
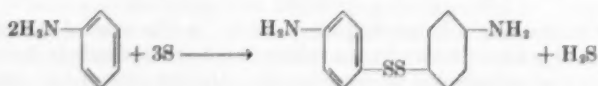


Naphthalene was found to react to some extent with sulfur at the α-position although it has poorer reactivity than the other model compounds.

## EXPERIMENTS AND RESULTS

### I. REACTIONS WITHOUT ZINC OXIDE

A mixture of 5 g. of model compound, 0.5 g. of sulfur, and 0.1 g. of accelerator was heated at 100–130° C, and the amounts of hydrogen sulfide evolved semiquantitatively examined by lead acetate paper. The results obtained are summarized as follows: (1) the largest quantity of hydrogen sulfide was observed in the reaction with aniline; (2) both cetylpyridinium bromide (CPB) and acetaldehyde-aniline (accelerator K) accelerated the formation of hydrogen sulfide. However, the accelerating effect of K is somewhat questionable, because hydrogen sulfide may be produced also by the reaction of sulfur and K itself. However, since K was found, in another experiment, to accelerate the reaction of masticated rubber and sulfur in dilute solution in the presence of zinc oxide, it seems reasonable to consider at least a part of hydrogen sulfide analyzed in the present experiment to be correlated to the accelerating action of K.

### II. REACTIONS WITH ZINC OXIDE

*Method.*—A mixture of 10 cc. of model compound, 0.5 g. of sulfur, 1.0 g. of zinc oxide, and 0.1 g. of accelerator was heated with stirring for a definite period (30 min. in most experiments). Tetralin was freed of peroxides by distillation. When two accelerators were used, the combined amount was 0.1 g. After the reaction the zinc sulfide formed was determined, and the percentage of sulfur converted into zinc sulfide to total sulfur used was calculated.

The reactions were carried out in air, in carbon dioxide, and in hydrogen. As the same results were obtained under the latter two gases, it can be said that these are inert in the present experiments.

*Analytical procedure.*—For practical application, the analytical procedure was simplified as much as possible.

The reaction mixture was filtered and washed with acetone. The precipitate was extracted with acetone in a Soxhlet apparatus, and the residue was transferred to a beaker together with the filter paper, to which 50 cc. of $0.1N$ sodium arsenite was added. The contents were acidified with hydrochloric acid to precipitate arsenic trisulfide, and the liquid was diluted to a volume of 250 cc. in a measuring flask together with the washings from the filter paper. Of this solution, 50 cc. was pipetted out and neutralized with sodium bicarbonate. Then the excess sodium arsenite was titrated with $0.1N$ iodine-potassium iodide.

The acetone extraction was complete when the three minute extraction cycle was continued for three hours. Even when the zinc salt of M (mercaptobenzothiazole), a very difficultly soluble compound, was used as an accelerator, no appreciable error was observed in this extraction procedure. The results with this accelerator will be reported elsewhere.

The reproducibility of the above procedure was excellent, and the deviation of the results, i.e., the percentage of sulfur in zinc sulfide to the total sulur, was $\pm 0.05$ per cent.

*Reaction of tetralin and sulfur in air.*—Amine and thiol accelerators were studied. As amine accelerators, K, diphenylguanidine (D), hexamethylenediamine (H), and CPB were used. The results are shown in Figure 1. As thiol accelerators, M, dibenzothiazoledisulfie . (DM), tetramethylthiuramdisulfide
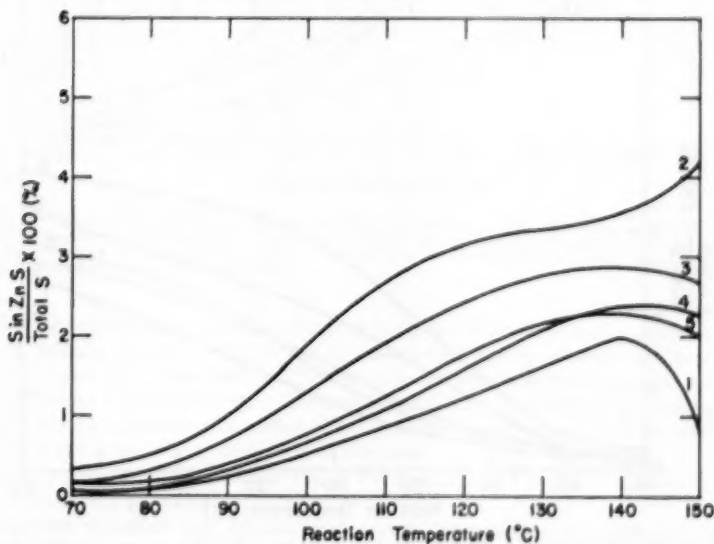


Fig. 1.—Reaction of tetralin and sulfur with amine accelerators. *1*—Nil; *2*—cetylpyridiniumbromide (CPB); *3*—diphenylguanidine (D); *4*—butyraldehydeaniline (K); *5*—hexamethylenetetramine (H).
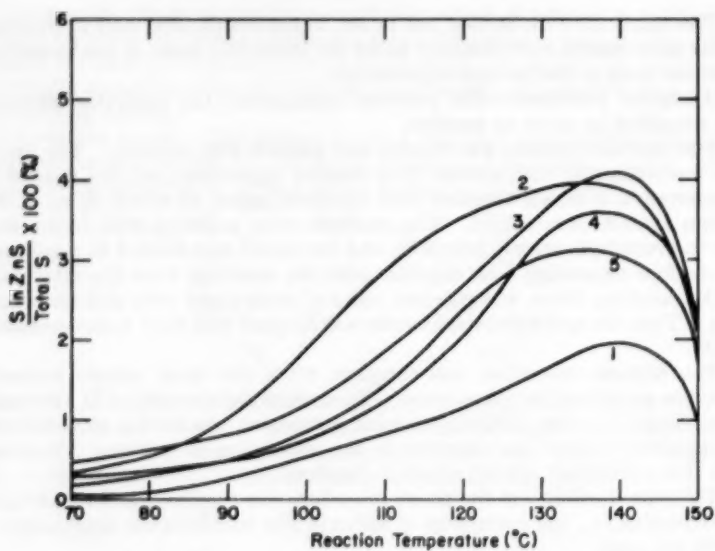
Fig. 2.—Reaction of tetralin and sulfur with thiol accelerators.  *1*—Nil; *2*—mercaptobenzothiazole & diphenylguanidine (mole ratio 4:3); *3*—tetramethylthiuram disulfide (TT); *4*—mercaptobenzothiazole (M); *5*—benzothiazolyldisulfide (DM).
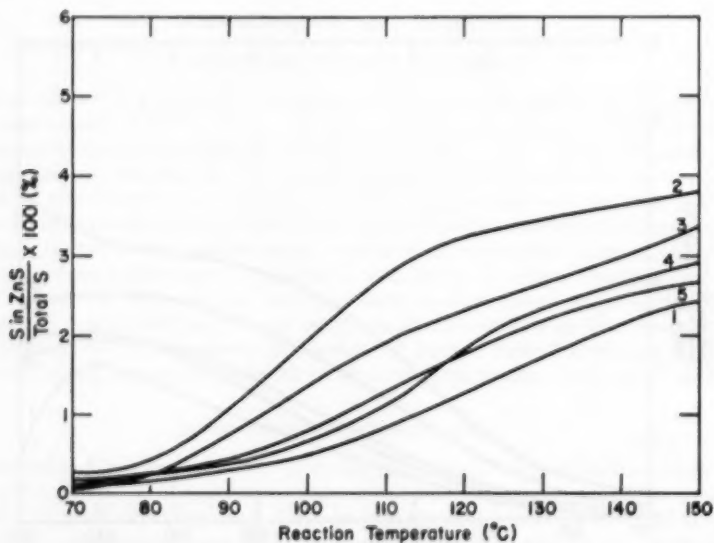


Fig. 3.—Reaction of tetralin and sulfur with amine accelerators in carbon dioxide.  *1*—Nil; *2*—cetyl-pyridiniumbromide (CPB); *3*—diphenylguanidine (D); *4*—butyraldehydeaniline (K); *5*—hexamethyl-enetetramine (H).

(TT), and a binary mixture, M + D (4:3) were studied. The results of thiol accelerators are given in Figure 2. The reaction time is 30 minutes unless otherwise stated.

The effects of accelerators other than CPB reached a maximum at 140° C and fell markedly at 150° C. The effect of CPB, however, increased considerably at 150° C. This is seen from the Figures in contrast to the results of the experiment in carbon dioxide, Figure 3.

*Reaction of tetralin and sulfur in carbon dioxide.*—The same accelerators as those in the preceeding experiment were used. The results are shown in Figures 3 and 4.

The differences between the results obtained in air and in carbon dioxide became pronounced at 120° C, and increased as the reaction temperature rose.
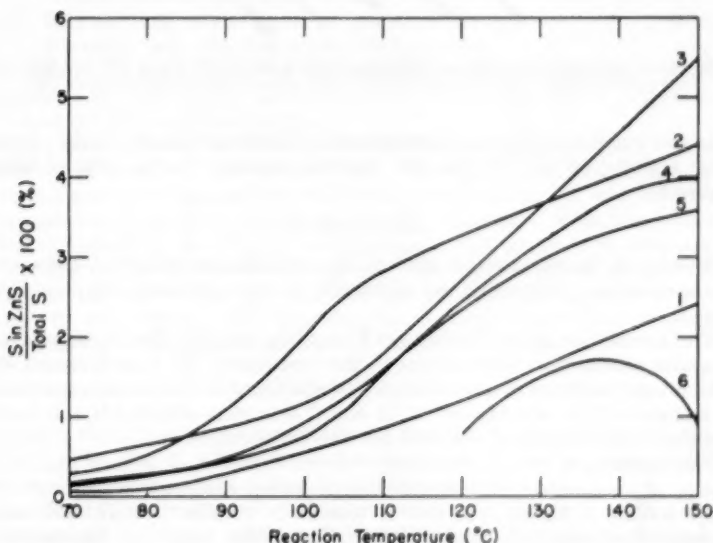


Fig. 4.—Reactions of tetralin and sulfur with thiol accelerators and of tetralin peroxide and sulfur without accelerator in carbon dioxide. 1—Nil; 2—mercaptobenzothiazole & diphenylguanidine (mole ratio 4:3); 3—tetramethylthiuram disulfide (TT); 4—mercaptobenzothiazole (M); 5—benzothiazolyldisulfide (DM); 6—tetralin peroxide (no accelerator).

*Reaction of tetralin peroxide and sulfur in carbon dioxide.*—As the model compound, tetralin peroxide, which was obtained by blowing oxygen into tetralin at 80° C for 4 hrs., was used. The peroxide content was 4.44 per cent which was determined by iodometry. The results of the reaction of this peroxide and sulfur without accelerator in carbon dioxide are given in Figure 4. The activity fell remarkably at 150° C as shown in Figure 4.

It may be suggested that the fall of the activity at 150° C is related to the formation of the peroxide of tetralin.

*Reaction of sulfur with toluene, xylene, aniline, phenol, chlorobenzene, o-dichlorobenzene, and naphthalene.*—In the reactions at 120° C, M and D showed marked accelerating effects as in the reaction with tetralin (Figure 5).
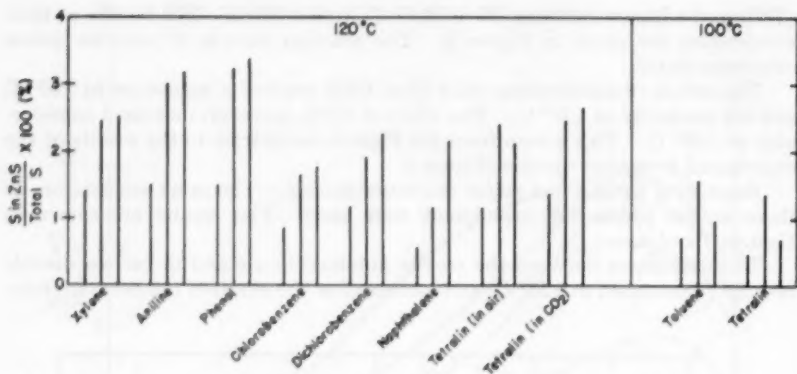
Fig. 5.—Reactions of sulfur and various model compounds in air at 120° C and 100° C.   Left column, blank; middle column, diphenylguanidine (D); right column, mercaptobenzothiazole (M).

In the reaction with o-dichlorobenzene without accelerator in air, decrease of the activity at 150° C was not observed contrary to the case of tetralin (Figure 6).

## DISCUSSION

A series of the experiments showed the remarkable similarities between reactions of rubber with sulfur and of tetralin or other aromatic compounds with sulfur.

The similarities are as follows: (1) The ability and the effective temperature of various accelerators were similar in the two cases; (2) a pronounced effect of the binary mixtures of accelerators was also found in the model experiments. For instance, 0.1 g. of a mixture of M and D was more effective in the reaction than the equal amount of either of the two accelerators.

*The reactivity of model compounds.*—From Figure 5, it is seen that, in the absence of accelerators, the reactivities of model compounds decrease in the order: aniline > phenol > xylene > toluene > tetralin > o-dichlorobenzene > monochlorobenzene > naphthalene.   The order may be interpreted in terms of the differences in the negativities of the relevant carbon atom caused
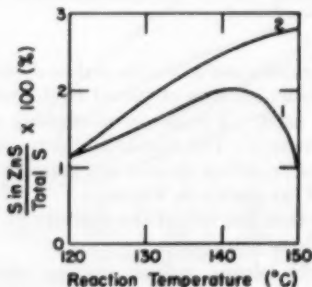


Fig. 6.—Reactions of tetralin and sulfur, and of o-dichlorobenzene and sulfur without accelerator in air.   1—Tetralin; 2—o-dichlorobenzene.

by various substituents and is approximately parallel to the order of the susceptibilities toward general cationoid reagents.

*The effect of air on the reaction of tetralin with sulfur.*—In the reaction of tetralin with sulfur in air a distinct drop in the yields of zinc sulfide was observed at 150° C. This may be ascribed to the effect of oxygen in air which oxidizes tetralin to form peroxide under the reaction conditions. On the other hand, no drop in the yield curve of zinc sulfide was observed in the vicinity of 150° C in the reaction of sulfur and o-dichlorobenzene which does not form a peroxide, Figure 6. Further, even under carbon dioxide, the distinct drop in the yield of zinc sulfide was again observed in reactions with tetralin involving a certain quantity of the peroxide.

According to the work of Yamada[12], tetralin peroxide is formed even at 100° C or below, but its decomposition is not significant until it is heated at 120–130° C. The peroxide decomposed violently at 150° C. These facts support the view that the drop in the yields of zinc sulfide was induced by the decomposition of tetralin peroxide, but not by its formation.

The following reactions may be made possible by the decomposition of tetralin peroxide: (1) Accelerator destruction; (2) Hydrogen sulfide oxidation to sulfur; and (3) Zinc sulfide oxidation.

Since the drop in the yields of zinc sulfide is observed in reactions with and without accelerators, (1) can be ruled out. Reaction (3) is also imporobable because the amount of zinc sulfide, which was formed at 140° C, was proved not to decrease even when it was heated at 150° C. A reaction of tetralin with sulfur was examined in air without accelerators. The amounts of zinc sulfide after heating at 140° C for 30 minutes and subsequent heating at 150° C for 30 minutes (A) was 0.0448 g. The amount after heating at 140° C for 30 minutes (B) was 0.028 g. The amount after heating at 150° C for 30 minutes (C) was 0.014 g. The sum of (B) and (C) is nearly equal to (A).

$$(A) \cong (B) + (C)$$

The latter is slightly larger because it takes 4 minutes to elevate the temperature from 140° C to 150° C. From these considerations, it may be concluded that Reaction (2) is most operative in the present conditions.

*The effect of tetralin peroxide and the properties of accelerators.*—With amine accelerators, D, K, H and others, only a small drop in the yield of zinc sulfide was observed, which indicated the inhibiting action of the amines against the oxidation. On the other hand, in the presence of CPB, the yield at 150° C was larger in air than in the carbon dioxide atmosphere. The cause of the accelerating effect of oxygen in this case is obscure because the acceleration mechanism of CPB in vulcanization is unknown; but this may be considered to have some correlation with the plasticizing action of CPB[12].

*The action of oxygen on rubber.*—It has been described previously that rubber is converted into its peroxide by oxygen in air as in the case of tetralin. It is believed that an active radical, which is formed by the decomposition of the peroxide, attacks a molecule of rubber and decomposes it through a chain mechanism[9]. In practical vulcanization, the chance of the oxidation of rubber is relatively small, and there is no evidence that the decomposition temperatures of the peroxides are identical in rubber and tetralin. However, it seems possible to suppose that there is some relation between the optimum temperature (140° C) of rubber vulcanization and the decomposition temperature of rubber peroxide.

*The relation between various model compounds and accelerators.*—Figure 5 shows the yields of zinc sulfide in the reaction, which was carried out at 120° C, under air and with or without accelerator such as D or M. The yields vary in the order: M > D > none. The order is valid for the reaction of tetralin under carbon dioxide, but it is reversed in the presence of air, which is accounted for by the effectiveness of D as an antioxidant.

## SUMMARY

1. To elucidate the chemical behavior of rubber toward sulfur, a series of experiments was carried out using model compounds: tetralin, toluene, xylene, aniline, phenol, chlorobenzene, dichlorobenzene and naphthalene. Similar reactivities between rubber and the model compounds were observed.

2. The effects of the accelerators in the reactions of the model compounds with sulfur were different according to whether or not zinc oxide was present in the reaction system.

3. A detailed examination of the quantities of zinc sulfide formed in the reaction of tetralin with sulfur in the presence of zinc oxide showed that several vulcanization accelerators have similar activating effects in rubber vulcanization.

4. With tetralin as reactant, the quantity of zinc sulfide decreased suddenly at the reaction temperature 150° C, which was ascribed to the rapid decomposition of tetralin peroxide at this temperature.

5. The accelerating action of CPB, contrary to that of the other accelerators, was promoted by tetralin peroxide.

6. Tetralin peroxide had only a small inhibiting influence upon reactions with the amine accelerators, which is ascribed to the antioxidative nature of the amine derivatives; the inhibiting influence becomes larger in reactions with thiol derivatives or without any added accelerators.

7. Substituent effect on the hydrogen abstraction of the model compounds was primarily determined by the negativity of the relevant carbon atom. The order of the reactivity was found to be in accord with that toward the general "cationoid reagents".

8. Analytical methods during and after the reactions were simplified for industry use.

## SYNOPSIS

The reactivities of several model compounds with sulfur were studied. The model compounds examined were aromatic compounds such as tetralin, aniline, phenol, chlorobenzene, toluene, xylene and naphthalene, which were considered to have reactivities similar to that of rubber with sulfur. Above all, tetralin was examined in more detail, because it is neutral and its boiling point is higher than the ordinary vulcanization temperature of natural rubber.

The experimental results are as follows: (1) some accelerators promote the reaction of the model compounds with sulfur to release hydrogen sulfide, irrespective of the addition of zinc oxide; (2) in the presence of zinc oxide, the formation of zinc sulfide was enhanced by each accelerator, a degree of acceleration which was in good accord with that in the case of rubber; (3) in the reaction between tetralin and sulfur under air, the formation of zinc sulfide decreased suddenly at 140° to 150° C, which was attributed to the action of tetralin peroxide; (4) naphthalene, which had been held to be inactive toward

sulfur, was found to react with sulfur below the temperature for rubber vulcanization.

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# THE MECHANISM OF ACCELERATOR ACTION *

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## INTRODUCTION

In the year 1839, Goodyear discovered that, on treatment with sulfur at elevated temperatures, natural rubber loses its plasticity and becomes elastic. Around the time of World War I, it was discovered that the reaction of the sulfur with the unsaturated rubber hydrocarbons could be promoted by the action of so-called vulcanization accelerators. The reaction then takes place not only faster and at lower temperatures but, in addition, one also needs less sulfur and the vulcanizates acquire considerably better technical properties. Accordingly a tremendous number of compounds have been examined as accelerators of vulcanization and much effort has been applied to develop accelerators with the most satisfactory properties. Today, accelerators are known which permit vulcanization at room temperature. In the past, the mechanism of accelerator action has been studied mostly with the methods of organic and physical chemistry. In the following, an attempt will be made to consider the problem from the viewpoint of the inorganic chemist.

One can attempt to interpret the catalysis from two points of view. Either the reactivity of the unsaturated natural rubber hydrocarbon is enhanced, or the sulfur will be converted into a more reactive form. Twiss[1] concluded from his investigations that the latter possibility is the more likely. Subsequently, this assumption has been supported by further observations. In particular, the discovery of Peachey[2] pointed in this direction, since natural rubber is vulcanizable at room temperature if it is treated successively with hydrogen sulfide and sulfur dioxide gases. The sulfur which is formed by this reaction is in the nascent state and is very reactive.

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

Based on this behavior, one would expect the so-called accelerators to react with sulfur in some way to form reactive sulfur intermediates. During our investigations in the field of metalloids[3], and especially of sulfur[4], we found reactions which are catalyzed by the basic nitrogen-containing group of accelerators. Subsequently, we diverted our studies toward the primary reactions of sulfur with other important types of accelerators. Our investigations are at that stage where we feel justified in releasing our tentative findings.

## CATALYSIS OF PHASE TRANSITIONS OF SULFUR

Those forms of sulfur which are soluble in organic media, for example rhombic sulfur, are composed of eight-member rings, the shape of which were determined by Warren and Burwell[5] with x-ray methods. The energy of a single bond between two sulfur atoms of the ring is listed as 63.8 kcal./mole, which is a very large value. When molten sulfur is quenched, one obtains, in addition to some soluble sulfur, a greater or lesser amount of a modification,
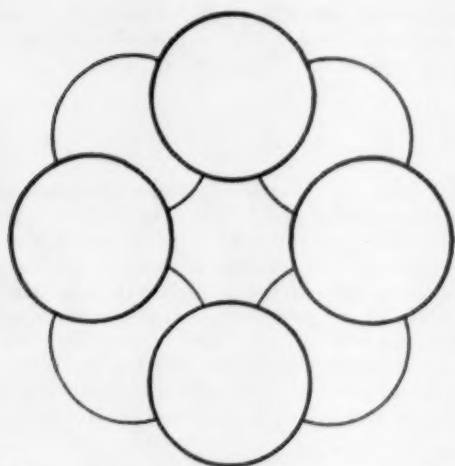
Fig. 1.—$S_8$-Ring according to Warren and Burwell. The distance between two sulfur atoms is 2.12Å. The bond angle is 106°.

which is insoluble in all solvents. For a number of reasons, this (insoluble) form is believed to consist of high molecular rings and not of open chain-like structures as is usually indicated in the literature. The number of atoms in these rings amounts to about 5000 according to the estimates of H. Specter[6]. It may be assumed that the bounding energy between two sulfur atoms in the many membered ring is of the same order as that in the eight-membered ring. If one wants to convert the insoluble sulfur into soluble sulfur, it is first necessary to break the ring at some spot. This can be done thermally or catalytically.

On account of the high bond strength, thermal cracking starts only at elevated temperatures. In boiling toluene (b.p., 111°), one observes a slow dissolution of the insoluble sulfur indicating that thermal dissociation of the S—S bond is evidently occurring.

The catalytic transformation can, for example, be brought about by sulfide ions. According to an old observation of Smith and Holmes[7], one needs only to bring insoluble sulfur in contact with sodium sulfide solution to make it soluble. The high susceptibility to this catalysis is especially evident if one adds sulfide ions to molten sulfur, for example in the form of potassium sulfide. It is then impossible to obtain insoluble sulfur even with the fastest quenching[7].

The rupture of the ring is facilitated because of the intermediate formation of polysulfide ions[4].

$$S^- + (S_x)_{Ring} \longrightarrow {}^-S\cdots\cdots S^-$$

The polysulfide chains have very reactive free ion groups at the ends. On account of the coiled structure of the chain, one end atom can easily be located in the vicinity of another atom of the same chain and can react at that site. Then a small ring, preferably $S_8$, is split off and the chain becomes shorter.
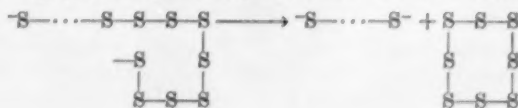
This reaction continues with successive splitting off of small rings until an ion end group reacts with another ring, splits that ring and connects with it, thus increasing the length of the newly formed chain.

$$-S\cdots-S^- + S-\cdots \quad \quad -S-\cdots-S-S-\cdots$$
$$\quad\quad\quad\quad | \quad : \longrightarrow \quad\quad\quad\quad\quad :$$
$$\quad\quad\quad\quad S-\cdots \quad\quad\quad\quad\quad\quad -S-\cdots$$

The increase and decrease in chain length under simultaneous splitting off of smaller rings continues further until finally dynamic equilibrium is reached between the $S_8$ rings which are stable at room temperature and the remaining polysulfide ions. The sulfur or, actually, polysulfide ions start a kind of chain reaction in which they continue to function since they cannot disappear.

Basic amines represent another very reactive group for the transformation of high molecular weight rings into $S_8$ rings[4]. Insoluble sulfur dissolves virtually instantaneously in carbon disulfide or benzene if a single drop of a basic amine is added to the suspension. To explain this phenomenon, we postulate that amine polysulfides of betaine-like structure are formed as an intermediate stage.

$$\begin{array}{ccc} R & & R \\ | & & | \\ R-N + (S_8)_{Ring} \longrightarrow R-N^+ \longrightarrow S-\cdots-S^- \\ | & & | \\ R & & R \end{array}$$
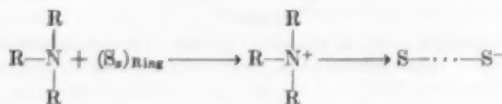
This reaction we want to describe in more detail. The elements in the right corner of the periodic system have a pronounced tendency to build into their outer shell eight electrons as four pairs. As an example, in the formation of sodium chloride, NaCl from sodium and chlorine atoms, a chlorine ion is formed when a chlorine atom with seven outer electrons abstracts the single outer electron from a sodium atom.

$$Na\cdot + \cdot Cl \longrightarrow Na^+ + Cl^-$$

In this formula, a dot refers to an unpaired electron (also called a lone electron) and a dash, an electron pair. The completion of the outer shell can also take place when two atoms share electrons to form an electron pair thus forming a covalent bond. This is the manner in which two chlorine atoms combine to form a chlorine molecule.

$$|\overline{Cl}\cdot + \cdot \overline{Cl}| \longrightarrow |\overline{Cl}-\overline{Cl}|$$

The purely thermal splitting of the sulfur ring can be effected in two ways. In one, homopolar scission, at the point of rupture, the bonding electron pair is split into two single electrons. An open chain is formed, and end atoms each having a lone electron in a reactive form with a tendency to pair. The end atoms, therefore, have free valences and are free radicals.

$$\begin{array}{c} S-S \longrightarrow \cdot S-\cdots-S\cdot \\ | \quad | \\ \cdot\cdot \end{array}$$
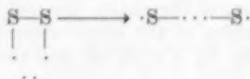
It can also happen that the bonding electron pair remains with one atom as the result of ionic scission. This atom at one end of the chain then has a negative charge and holds four electron pairs. The sulfur atom at the other

end holds only three electron pairs and, with respect to the nucleus, lacks one electron and is, therefore, positive.

$$\overset{S—S}{\underset{\cdot\ \ \cdot\cdot}{|\quad|}} \longrightarrow {}^+S\!-\!\cdots\!-\!S^-$$
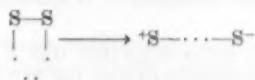
Experience shows that the energy for the formation of an isolated electron (ionic scission) is very large so that this sort of splitting does not happen easily. If one now adds some material which tends to donate an electron pair, this electron hole can be filled and an ammonium polysulfide is formed. Such a material is an Ansolvo base (Lewis base), the main representatives of which are amines.

$$R_2N + \overset{S—S}{\underset{\cdot\ \ \cdot\cdot}{|\quad|}} \longrightarrow \overset{+}{R_2N} \longrightarrow \overset{=}{S}\!-\!\cdots\!-\!S^-$$
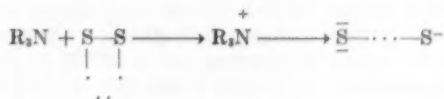
In the above equation, the arrow on the right indicates a bond in which the bonding electron pair comes from one atom, the nitrogen atom. Such a bond is called semipolar. The amine oxides and the boron fluoride ammonia complex are typical representatives which owe their composition to such bonds.

$$\underset{R}{\overset{R}{R—N}} \longrightarrow O \qquad\qquad \underset{H}{\overset{H}{H—N}} \longrightarrow \underset{F}{\overset{F}{B—F}}$$
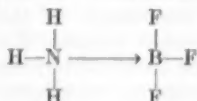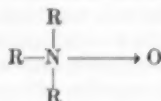
The splitting of the sulfur ring is facilitated through this reaction since the energy for formation of an isolated electron actually does not have to be supplied. The rate of change of insoluble sulfur into soluble form effected by amines can be explained best as a chain reaction. Both ends of the opened chain are very reactive and can behave as ionic ends which can be explained by the following equations:
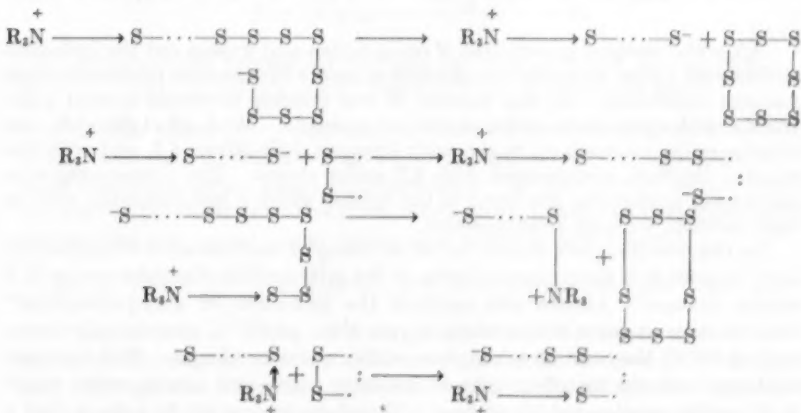
Accordingly, a chain reaction is initiated through the formation of an ammonium polysulfide which continues until the two ends of a single chain find each other and unite with the splitting off of the amine and the formation of a ring.

### THE AMINE AND SULFIDE ION CATALYZED TRANSFORMATION OF SULFUR

The mechanism of ring scission described above should also apply to other chemical reactions of sulfur. To verify this, we first investigated the formation of trithion from anethole and sulfur.

$$H_3C-O-\langle\rangle-CH=CH-CH_3 + 5/8(S_8) \longrightarrow$$

$$H_3C-O-\langle\rangle-C=C \begin{smallmatrix} H \\ \\ C=S \end{smallmatrix} + 2H_2S$$
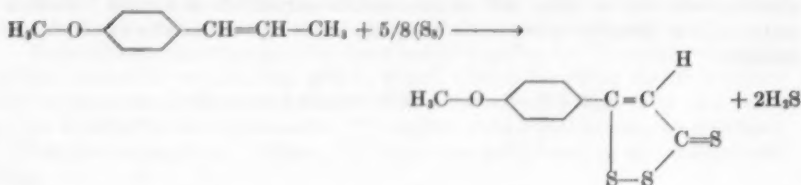
The reaction begins in the molten stage at 170° C and proceeds at a practical rate at 220° C[8]. In the presence of a few drops of tributyl amine this reaction takes place in boiling toluene. The trithion formation can even be demonstrated in boiling benzene. It was further observed that the catalytic efficiency increases with the basicity of the amine. With this reaction, it cannot be definitely established whether it is the amine which acts catalytically or the sulfide ions which are formed by reaction of the hydrogen sulfide with the amine.

For this reason, we investigated the catalytic reaction of organic disulfides with sulfur[9]. Alkyldisulfides (for example methyl disulfide) do not react even at the boiling point with elementary sulfur. But, if one adds a trace of sulfide ions, for example by the addition of one drop of amine and a few bubbles of hydrogen sulfide, a fast reaction takes place at room temperature. The sulfur becomes soluble through the formation of alkylpolysulfides.

$$H_3C-S-S-SH_3 + \frac{x}{8}(S_8) \xrightarrow{S^-} H_3C-S-S_x-C-SH_3$$
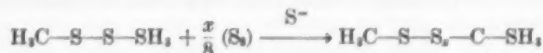
After the reaction is complete, if one acidifies and washes out the hydrogen sulfide with water, then one can partially separate the reaction product by high vacuum distillation. In this manner, it was possible to obtain methyl polysulfides with up to seven sulfur atoms per molecule. With ethyl disulfide, one obtains sulfur contents up to six, with dipropyl derivatives, 4.5, and with the n-butyl disulfide, a compound with 4.2 sulfur atoms. The components containing the most sulfur are found in the residue which is not distillable, even in high vacuum, without decomposition.

In this reaction, one should not alone consider the formation of polysulfide ions, because it is likely that splitting of the intermediate disulfides occurs in a similar manner. Amines also catalyze the formation of alkylpolysulfides[9]. The reaction at room temperature is very slow, at 50° C considerably faster, and, at 90° C, the reaction takes place within about two hours. This behavior contrasts with the transformation of insoluble sulfur into soluble sulfur which is so greatly accelerated by amines. Therefore, we are led to believe that a

chain reaction is initiated by the amine only in the latter case—not in the first.

$$H_3C—S—S—CH_3 + S^- \longrightarrow H_3C—S^- + {}^-S—S—CH_3$$

The same transformations catalyzed by sulfide ions or amines can be obtained with aromatic disulfides and with tetramethylthiuram disulfide, but the separation of the components is generally not possible in this case.

Langenbeck[10] has already proven that tetramethylthiuram disulfide and sulfur react with each other in the presence of pyridine. He found that the solubility of the mixture of the components in pyridine is about twice as large as the sum of the solubilities of the single components in this solvent. In this case, the solvent, pyridine, acts as a catalyst for the transformation of disulfides into polysulfides.

The examples chosen show clearly that, in general, sulfide ions and amines affect catalytically the reactions of elementary sulfur. One has to accept that the vulcanization of rubber in the presence of amines, as introduced by Hofmann and Gottlob[11], is dependent upon this phenomenon of ring splitting. Here one finds, as with trithion formation, an increase in acceleration with an increase in basicity of the amine[11,12]. Only thorough investigations can show to what extent the amine, itself, or the sulfide ions, formed in small amounts through side reactions during vulcanization, is responsible for acceleration; since potassium hydroxide or sodium hydroxide[1,12], which act as accelerators, readily form sulfide ions on vulcanization.

We should not overlook research which led to theories which touch on the above considerations and findings. Thus, Kratz, Flower and Coolidge[13] supposed that amine and sulfur form amine monosulfide, $R_3NS$, as an intermediate which donates its sulfur in active form. Van Alphen[14] recently referred to the tendency of the lone electron pair of the nitrogen atom in an organic base to form a semipolar bond. Bedford[15] has shown that sulfur reacts with the impurities of rubber, especially proteins, forming hydrogen sulfide. Accordingly, reactive polysulfide ions are formed from amines, hydrogen sulfide and sulfur. According to the theory of Gordon[16], an accelerator can decompose into radicals $(Z \cdot)$ which open sulfur rings, forming sulfur chains with a very reactive radical-like end.

$$Z \cdot + (S_8)_{Ring} \longrightarrow Z—S—\cdots—S \cdot$$

## ATTEMPTED INTERPRETATION OF THE ACTION OF SULFUR-CONTAINING ACCELERATORS OF VULCANIZATION

For over thirty years, lead and zinc salts of xanthic acid, dithiocarbamic acid or mercaptobenzothiazole have been extensively used as accelerators. In most cases, amines are added simultaneously. Bedford[15], who had an important part in the development of these accelerators, considered that intermediate polysulfides are formed which release their sulfur in active form:

$$(R—S—)_2Zn + 2xS \longrightarrow (R—S—S—)_2Zn \longrightarrow (R—S—)_2Zn + 2xS_{(Active)}$$
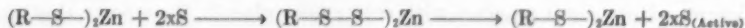
With the aim of finding an intermediate reaction between these salts and sulfur, we thoroughly investigated the structure of the lead and zinc compounds and their general behavior. Here one deals, as the inorganic chemist well knows, not with ordinary salts but with so-called inner-complex salts. This is

shown by their solubility in organic media.    Zinc xanthate should be written:

$$R-O-C\underset{S}{\overset{S}{\diagup}}Zn\underset{S}{\overset{S}{\diagdown}}C-O-R$$
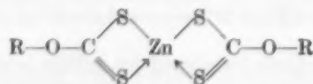
Here the four sulfur atoms surround the zinc in the shape of a tetrahedron. The bonding takes place through shared electron pairs with two sulfur atoms held by covalent bonds and the other two by semipolar bonds.

The complex salt contains two ring systems, each consisting of four members—a carbon, a zinc and two sulfur atoms.    The experience of the organic chemistry indicates that such four-membered rings are unstable and hence easily ruptured.    This can be demonstrated by pyridine addition which leads to the formation of compounds in which two pyridine molecules have replaced the two semipolar bonded sulfur atoms[17].

$$R-O-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{N}{\uparrow}}{\overset{\overset{N}{\uparrow}}{Zn}}-S-\underset{\underset{S}{\|}}{C}-O-R$$
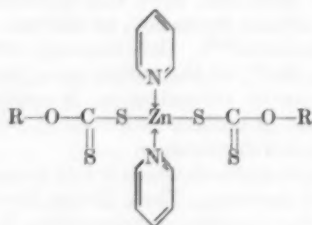
The low stability of the ring system shows up also in the following:

$$Co\left[\underset{S}{\overset{S}{\diagup}}C-O-R\right]_3 \quad \text{and} \quad Co\left[\underset{S}{\overset{S}{\diagup}}C-NR_2\right]_3$$
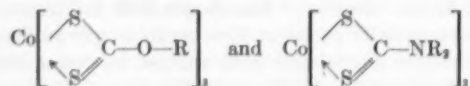
Xanthates and dithiocarbamates of the trivalent cobalt, which are separable into optical antipodes, racemize at room temperature, while cobalt complexes with three five-membered ring systems begin to do this at about 100° C.

We assume that the instability of the four-membered rings is connected in some way with the activation of the sulfur insofar as the ring (intermediately) breaks to give:

$$R-O-\underset{\underset{S}{\|}}{C}-S-Zn-S-\underset{\underset{S}{\|}}{C}-O-R \quad \text{or} \quad R-O-C\underset{S}{\overset{S}{\diagup}}Zn-S-\underset{\underset{S}{\|}}{C}-O-R$$
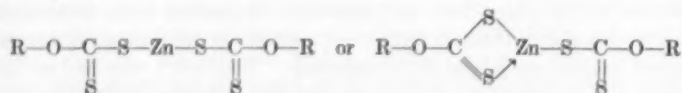
The zinc atom is then coordinately unsaturated and seeks to utilize its unused valences.    How can a reaction with sulfur take place?    To answer this question, certain experimental investigations[19] have been conducted.

When sulfur and zinc xanthate or dithiocarbamate are dissolved in benzene, no reaction is observed at room temperature.    On boiling, only a very faint yellowing slowly occurs, which could be derived from impurities.    A more intense yellowing occurs at room temperature if the components are dissolved in

pyridine instead of benzene. The material responsible for the discoloration cannot be isolated.

When zinc phenylmercaptide and sulfur are dissolved in pyridine at room temperature, an intense yellow solution is obtained immediately. A yellow amorphous powder of somewhat varying composition can be precipitated from this solution with water or alcohol. An analysis is given below. Apparently, in these substances a part of the mercaptan groups have been replaced by polysulfide sulfur. Diphenyl disulfide can be detected in the filtrate.

### Isolated Mercaptide-Polysulfide

$Pb_1S_{2.1}(S\!-\!\langle\ \rangle)_{0.12}$  $Zn_1S_{1.9}(S\!-\!\langle\ \rangle)_{0.08}(NC_5H_5)_{0.6}$

$Sn_1S_{3.0}(S\!-\!\langle\ \rangle)_{0.06}(NC_5H_5)_{0.9}$  $Cd_1S_{2.1}(S\!-\!\langle\ \rangle)_{0.07}(NC_5H_5)_{0.6}$
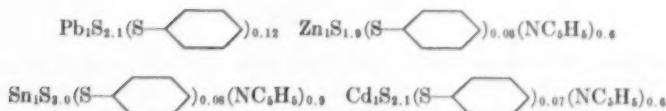
A similar reaction is observed with the cadmium phenylmercaptide and the tin salt of thiophenol, but the mercaptide-polysulfides of these metals are difficultly soluble and readily precipitate by themselves. It is not necessary to add water or alcohol.

If one starts with the lead phenylmercaptide, one first observes a red color— then the formation of a precipitate which becomes black since it decomposes to form lead sulfide. If one works at −20° C, it is possible to isolate and analyze a red precipitate. Again, one finds a mercaptide-polysulfide which is more unstable and is converted to lead sulfide at room temperature. This conversion is especially fast in the dry condition. The zinc mercaptide polysulfide is considerably more stable and does not revert to zinc sulfide, even at 100° C. This varying stability can also be observed with vulcanization. Stiehler and Wakelin[20] showed by x-rays that lead containing accelerators are transformed during vulcanization into lead sulfide. With those containing zinc, no zinc sulfide is formed.

The mercaptide residue of the red mercaptide-polysulfide of lead can be replaced with halogen by treatment with dilute hydrogen halides. These mixed halide polysulfide compounds of lead are already well known. K. A. Hofmann[21] obtained them in 1904 from lead halide solutions by reaction with yellow ammonium (poly) sulfide.

The reaction between sulfur and lead phenylmercaptide in pyridine solution represents a very sensitive and convenient test for sulfur. Even $1\gamma/cc$ of sulfur can be detected.

The behavior of mercury phenylmercaptide is very interesting. In contrast to the other named phenylmercaptides, it is soluble in benzene. In this medium, no reaction occurs at room temperature at first but after one week, one observes a small amount of yellow-brown precipitate. In pyridine solution, a black mercury sulfide is instantly formed. No reaction was observed at −15° C and slow warming leads to a yellowing, probably caused by a mercaptide-polysulfide; at −5° C the black mercury sulfide is obtained.

All these reactions show that, in the presence of pyridine, a very fast reaction takes place between the phenylmercaptides of zinc or lead and sulfur which occur in the absence of pyridine only very slowly, if at all. We choose to assume

that the splitting of the sulfur ring occurs according to the following scheme.

$$S-Zn-S \quad + (S_8)_{Ring} \rightleftharpoons$$

$$S-Zn-S \rightleftharpoons \quad \begin{array}{c} \text{Mercaptide-Polysulfide} \\ + \\ \text{Disulfide} \\ + \\ \text{Pyridine} \end{array}$$
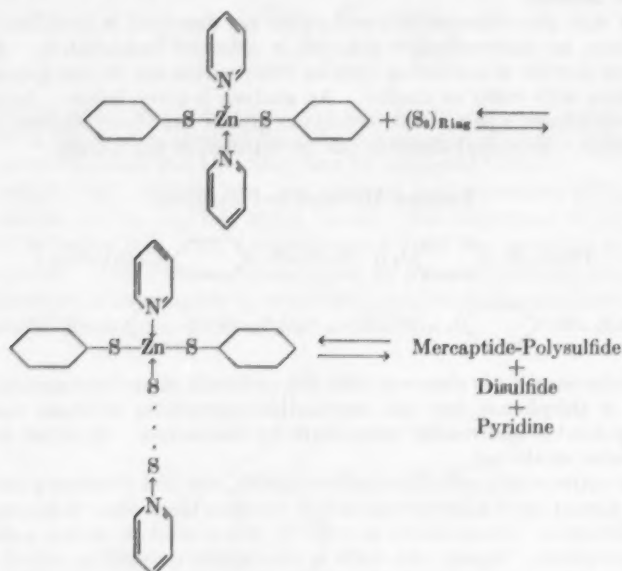
Zinc phenylmercaptide dissolves in pyridine because two solvent molecules can easily attach themselves to the "coordination unsaturated" zinc atom but the bonds holding the resulting complex together in turn can be easily broken. The dissociation products in turn react with the sulfur ring, the splitting of which becomes easy since both ends—the negative and also the positive—are stabilized through reaction with the zinc atom and the pyridine molecule derived from the complex. This intermediate product has active sulfur and, therefore, can react to form mercaptide-polysulfide.

In the vulcanization of rubber, one usually uses zinc salts of xanthic acid, dithiocarbamic acid, or of mercaptobenzothiazole and adds organic bases. These inner complex salts have the advantage of being soluble in raw rubber, while zinc phenylmercaptide is insoluble. One must assume the following equilibria:

$$R_2N-C \underset{S}{\overset{S}{<}} Zn \underset{S}{\overset{S}{>}} C-NR_2 \quad \overset{NR_3}{\rightleftharpoons} \quad R_2N-C \underset{S}{\overset{S}{<}} Zn \cdots C-NR_2 \quad \overset{(S_8)_{Ring}}{\rightleftharpoons}$$

$$R_2N-C \underset{S}{\overset{S}{<}} Zn \underset{S}{\overset{S-C-NR_2}{>}} \quad \rightleftharpoons \quad \text{Mercaptide-Polysulfide}$$

$$S \longleftarrow NR_3$$

and/or

$$R_2N-C\overset{S}{\underset{S}{\diamond}}Zn\overset{S}{\underset{S}{\diamond}}C-NR_2 \overset{NR_3}{\underset{\longleftarrow}{\longrightarrow}} R_2N-C\overset{\overset{NR_3}{|}}{\underset{\parallel}{S}}S-Zn-S-C-NR_2 \overset{(S_8)_{Rings}}{\longleftarrow}$$

$$R_2N-C\overset{NR_3}{\underset{\parallel}{S}}S-Zn-S-C-NR_2 \rightleftarrows \text{Mercaptide-Polysulfide}$$

$$S \longleftarrow NR_3$$
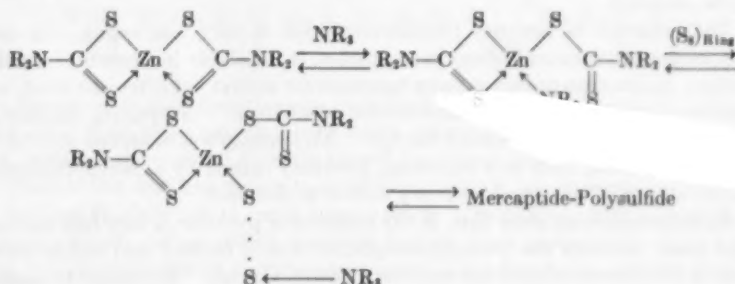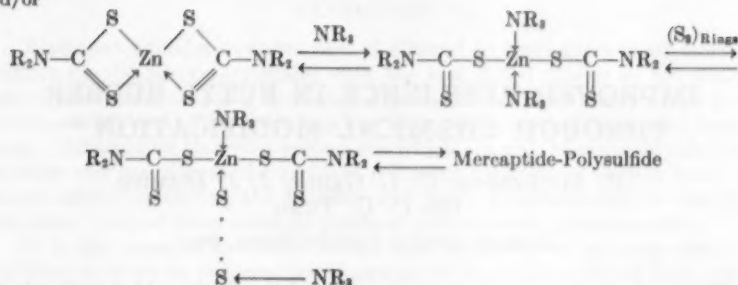
The zinc complexes, together with the sulfur, when dissolved in pyridine, give only a faint yellowing. The complex salt formation favors the left side of the equation. But still, sufficient polysulfide sulfur is formed to be transferred to the rubber molecule.

Besides the zinc compounds and amines, one adds to the vulcanization mixture so-called zinc soaps which are generally zinc palmitate or stearate. These substances also react in pyridine solution with elementary sulfur, and one observes a faint yellowing. If one adds, simultaneously, carbon disulfide, one obtains much more intense yellowing.

Even zinc oxide, which is widely used in vulcanization, reacts when dispersed in pyridine with sulfur if carbon disulfide has been added. A yellowing occurs; and, at the same time, zinc oxide goes into solution. Certainly, polysulfide compounds of zinc must be present.

With this scheme, we believe we have pointed out the primary reaction of the sulfur in the presence of organic bases with the zinc- and lead-containing accelerators. The intermediate product, and also the more stable mercaptide-polysulfide, contain reactive sulfur which can react with the isoprene chains of the raw rubber.

We have not investigated the slower reaction of the sulfur with the above named metal compounds in the absence of organic bases enough to permit us to treat them further at this time.

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# IMPROVED RESILIENCE IN BUTYL RUBBER
## THROUGH CHEMICAL MODIFICATION *

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The relatively low chemical unsaturation of the Butyl rubber molecule has long provided an incentive to rubber compounders to utilize this property for the resistance it contributes to degradation by heat, light, oxygen, and ozone. Unfortunately this low unsaturation has been a limiting factor in development of the proper balance of physical properties in Butyl rubber vulcanizates for satisfactory performance in applications where heavy dynamic work is imposed as, for example, in tire service.

This paper discusses a new approach toward improving the properties of Butyl rubber vulcanizates: namely, that of chemical modification of the Butyl polymer by a substituted polyfunctional aromatic amine. This chemical modifier is N-methyl-N,4-dinitrosoaniline and is currently available in 33⅓ per cent active mixture with inert filler under the trade mark Elastopar[1]. The use of Elastopar modifier in Butyl rubber leads to greatly improved resilience and associated properties, increased 300 per cent modulus, decreased Shore hardness, enhanced processing characteristics, improved low-temperature properties, and increased electrical resistivity of several orders of magnitude.

The past three years have witnessed some remarkable advances in the technology of processing Butyl rubber by virtue of work reported by Gessler and coworkers[2-6] on promoted heat treatment of mixtures of Butyl rubber with carbon black and silica, respectively. Butyl rubber vulcanizates with greatly improved resilience were produced by repeated cycles of heating and remilling or by prolonged mastication of the Butyl-carbon black masterbatch.

Two promoters for the heat-influenced interaction between polymer and carbon black were proposed, sulfur and p-dinitrosobenzene. The processing involved: (a) mixing of the carbon black and promoter into the polymer under conditions which produce good dispersions; (b) Banbury mastication of the resulting mixtures for 10–30 minutes at 300–400° F; and (c) completion of compounding and vulcanizing in accord with customary factory practice. Certain disadvantages are inherent in these conditions. The use of p-dinitrosobenzene involves a lengthy mixing cycle. The promoter itself, moreover, has a well-known tendency to form crosslinks between Butyl polymer chains; this can be an undesirable side reaction, affecting adversely the processibility of the resulting mixed stock.

This currently reported work discusses data which attest to the effectiveness of Elastopar in improving the properties of Butyl rubber vulcanizates without the accompaniment of decreased processibility. Reaction can be carried out in a Banbury mixer under normal conditions of operation and, indeed, has been demonstrated successfully on a plant scale.

## EXPERIMENTAL

Elastopar modifier operates best if allowed to react for a short time (one minute on the laboratory scale) with the raw Butyl rubber in the Banbury mixer; carbon black and vulcanizing ingredients are then incorporated in conventional fashion.    This procedure was followed for most of the studies reported here.    Alternative Banbury procedures which are also effective involve introduction and reaction of the additive following blending of carbon black with Butyl rubber or adding the modifier and black simultaneously to the Butyl polymer.    Any of these could be practical procedures in plant operation.

It is also possible to obtain comparable improvement in properties if the modified polymer be prepared by dispersion of the additive in raw Butyl rubber on the mill, followed by static oven heating of the Butyl-modifier mixture to effect reaction.

A considerable part of the experimental work consists of studies of the use of this new modifier at various concentrations (0.0–3.0 parts/100 Butyl rubber) in recipes containing 50 parts of medium processing channel black or high abrasion furnace black, respectively.    In the investigation of other variables, a reinforcing system consisting of a 35/15 mixture of MPC and HAF blacks was used.

Unless otherwise indicated, compounding recipes, mixing techniques, and curing conditions are as shown in Table I.    Total Banbury mixing time for

### TABLE I
#### BASIC RECIPE AND MIXING CONDITIONS

| Enjay Butyl* 217 | 100.0 | Add to preheated Banbury— |
| Elastopar | 0.0–3.0 | 300° F. Mix 1 minute |
| Carbon black | 50.0 | Mix 9 minutes/300° F |
| Stearic acid | 1.0 | |
| Zinc oxide | 5.0 | |
| Thiofide† | 1.0 | Mix on mill/122° F |
| Thiurad‡ | 1.0 | |
| Sulfur | 2.0 | |
| | Cure 45 min./307° F | |

* Enjay Butyl—A registered trade mark of Enjay Co., Inc.
† Thiofide—A registered trade mark of Monsanto Chemical Co. (Benzothiazolyl disulfide).
‡ Thiurad—A registered trade mark of Monsanto Chemical Co. (Tetramethylthiuram disulfide.)

modification of the Butyl rubber and incorporation of the carbon black was arbitrarily set at 10 minutes for a considerable portion of the work described. This choice of cycle was made and used prior to a study which explored variations in times of mixing.    That a 10-minute period is longer than necessary is demonstrated by the data in Table V.

Processing and testing equipment, as well as procedures followed, are listed in Table II.

### RESULTS

*Modifier concentration.*—Table III describes the changes in stress-strain. Shore hardness, Mooney viscosity and scorch time, torsional hysteresis, and Goodrich flexometer data as the concentration of Elastopar is varied over the range of 0.0–3.0 parts.    It is striking that, in general, substantial increases in 300% modulus are accompanied by simultaneous decreases in Shore hardness. Optimum modulus and hysteresis properties are developed with a concentration range of 1.2–1.8 parts Elastopar modifier/100 Butyl rubber.    There are no

### TABLE II

### TEST METHODS AND CONDITIONS OF EVALUATION

| Operation or Test | Conditions |
|---|---|
| Banbury mixing | No. 00 Banbury |
| Mill mixing | 6 × 12 mill—roll speed ratio, 1.4:1 |
| Mooney viscosity | Large rotor—4 minutes running time at 212° F, ASTM D927-53T* |
| Mooney scorch | Total running time to reach a viscosity of 10 points above minimum value at 275° F, ASTM D1077-49T* |
| Stress-strain | ASTM D412-51T* |
| Torsional hysteresis | As described by Mooney and Gerke[7]— tests run at 77° F |
| Hardness | Shore A durometer—ASTM D314-52T* |
| Goodrich flexometer | 1800 cpm, 17.5-inch stroke, 175 psi. load, ambient temperature, 212° F, ASTM D623-41T* |
| Yerzley oscillograph | As described by Baldwin[8] |
| Electrical resistivity | Vibrating reed electrometer, Model 30, Applied Physics Corp. (unpublished method). |
| Low-temperature | Clash-Berg method, ASTM D1043-51* |

* American Society for Testing Materials, Philadelphia, Pa.

distinct trends in tensile strength, but the modified stocks generally show reduced ultimate elongations. A plot of 300% modulus versus time of cure in Figure 1 furnishes additional confirmation of the important changes which have taken place in the Butyl polymer.

### TABLE III

### PROPERTIES OF BUTYL RUBBER STOCKS VERSUS CONCENTRATION OF MODIFIER

| | Parts Elastopar/100 Butyl rubber | | | | | |
|---|---|---|---|---|---|---|
| MPC Black | 0.0 | 0.6 | 1.2 | 1.8 | 2.4 | 3.0 |
| Mooney viscosity (ML-4/212° F) | 95 | 89 | 94 | 102 | 100 | 91 |
| Mooney scorch (min. to 1+10) @ 275° F | 17 | 20 | 22 | 21 | 21 | 21 |
| 300% modulus (psi) | 1400 | 1800 | 1930 | 2000 | 1930 | 1980 |
| Ultimate tensile strength (psi) | 3150 | 3080 | 3150 | 3000 | 2790 | 2750 |
| Elongation (%) | 560 | 460 | 450 | 420 | 410 | 400 |
| Hardness (Shore A) | 67 | 64 | 60 | 62 | 60 | 64 |
| Torsional hysteresis (logarithmic decrement) @ 77° F | 0.404 | 0.247 | 0.174 | 0.166 | 0.176 | 0.174 |
| Goodrich flexometer data @ 212° F | | | | | | |
| Dynamic drift (%) | 17.7 | 14.4 | 14.1 | 13.6 | 14.8 | 16.4 |
| Permanent set (%) | 20.6 | 16.6 | 15.4 | 16.4 | 16.7 | 19.5 |
| Heat rise (° F) | 47 | 38 | 36 | 36 | 40 | 41 |
| HAF Black | | | | | | |
| Mooney viscosity | 93 | 85 | 90 | 75 | 82 | 84 |
| Mooney scorch | 17 | 19 | 18 | 20 | 17 | 16 |
| 300% modulus | 1590 | 2160 | 2440 | 2350 | 2410 | 2540 |
| Ultimate tensile strength | 2240 | 2600 | 2630 | 2550 | 2730 | 2540 |
| Elongation | 410 | 380 | 340 | 350 | 350 | 300 |
| Hardness | 74 | 74 | 70 | 70 | 69 | 74 |
| Torsional hysteresis | 0.397 | 0.322 | 0.239 | 0.215 | 0.186 | 0.263 |
| Goodrich flexometer data | | | | | | |
| Dynamic drift | 17.3 | 14.4 | 12.6 | 15.7 | 12.4 | 22.4 |
| Permanent set | 20.2 | 18.0 | 14.6 | 18.3 | 15.8 | 24.7 |
| Heat rise | 47 | 43 | 38 | 43 | 38 | 58 |
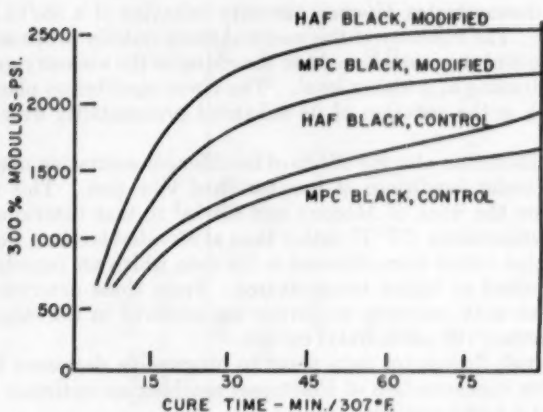
FIG. 1.—Modulus versus cure time for modified and control Butyl stocks.

The use of an additive which increases 300% modulus $1\frac{1}{2}$ to two-fold over that of the control might well be expected to introduce scorching problems. The data show that on the contrary this modifier effects an increase of 3–4 minutes in scorch time. Mooney viscosities of the fully compounded MPC black stocks are somewhat erratic, but those of the HAF stocks are definitely decreased as a result of chemical modification.
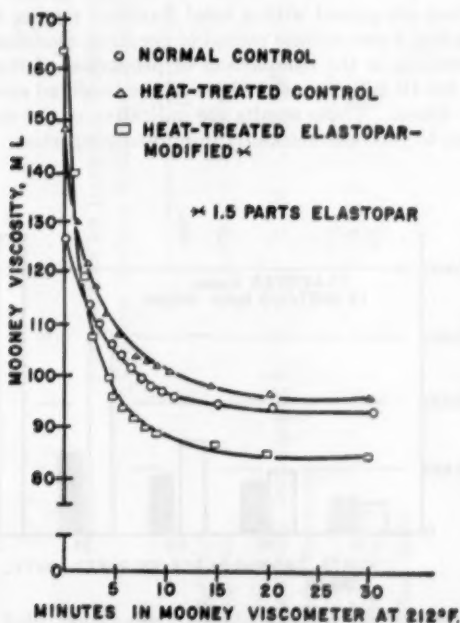


FIG. 2.—Mooney viscosities of normal, heat treated, and heat-treated Elastopar-modified, HAF/MPC Butyl rubber stocks.

Figure 2 demonstrates Mooney viscosity behavior of a 35/15 MPC/HAF black system. The viscosity of the modified stock quickly drops several points below the values of the control stocks in the course of the viscosity measurement, although originating at a higher level. The lower equilibrium plasticity of the modified stock is the criterion of its enhanced processibility over that of the controls.

Table III illustrates also the effects of modifier concentration upon resilience, as measured under conditions of free torsional vibration. This work differs somewhat from the work of Mooney and Gerke[7] in that determinations were run at room temperature (77° F) rather than at elevated levels. Consequently, somewhat higher values were obtained in the data which are reported here than would be obtained at higher temperatures. From these determinations it is again apparent that optimum properties are achieved in the range of 1.2–1.8 parts of Elastopar/100 parts Butyl rubber.

The Goodrich flexometer data point to progressive decreases in hysteresis with increasing concentration of Elastopar, reaching an optimum level in the range of 1.2–1.8 parts modifier.

*Modification temperature.*—The action of the modifier is observed to be strongly dependent upon temperature of reaction. The results shown in Table IV were obtained with 1.5 parts of the modifier per 100 parts of Butyl rubber, employing a 35/15 mixture of MPC/HAF black at the 50-part level. Temperatures of Banbury modification were varied over the range of 170–390° F; the respective temperatures were then maintained throughout incorporation of the carbon black. Optimum 300% modulus and torsional hysteresis properties are reached at a mixing temperature as low as 255° F.

*Mixing cycle time.*—The data in Table V show that optimum modulus and hysteresis properties are gained with a total Banbury mixing time as short as 2–3 minutes including a one-minute period of chemical modification.

Particularly striking is the comparison of properties of the blank control, which was mixed for 10 minutes, with those of the modified stocks, which were mixed for shorter times. These results are indicative of the speed with which the modifier reacts to produce markedly improved properties.
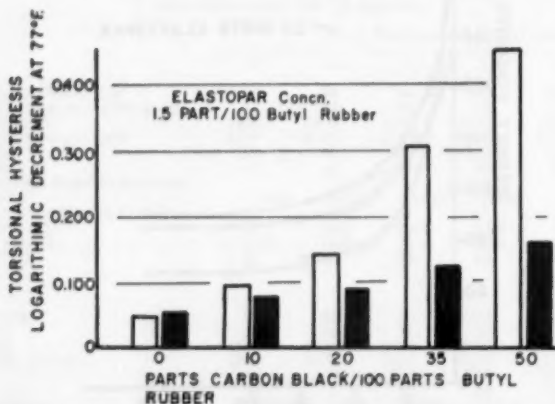


Fig. 3.—Effectiveness of modifier versus concentration of carbon black. Black bars give results for modified stocks; unshaded bars represent stocks without modifier.

TABLE IV

TEMPERATURE OF BANBURY MODIFICATION AND MIXING WITH CARBON BLACK

[Variation Banbury Modification Temperature (35/15 MPC/HAF Black Stocks)]

| | Mixing temperature, ° F | | | | | | |
|---|---|---|---|---|---|---|---|
| | 300* | 170 | 210 | 255 | 300 | 345 | 390 |
| Stress-strain | | | | | | | |
| $M_{300}$ (psi) | 1670 | 1700 | 1970 | 2130 | 2240 | 2280 | 2380 |
| Torsional hysteresis | | | | | | | |
| Logarithmic decrement @ 77° F | 0.426 | 0.250 | 0.282 | 0.197 | 0.196 | 0.175 | 0.175 |
| Goodrich flexometer | | | | | | | |
| Dynamic drift, % | 19.1 | 24.9 | 20.7 | 13.8 | 13.6 | 10.0 | 10.2 |
| Permanent set, % | 21.8 | 25.1 | 22.8 | 15.5 | 13.6 | 11.1 | 12.5 |
| Heat rise, ° F | 50 | 50 | 50 | 36 | 34 | 29 | 31 |

* Blank control.

TABLE V

TIME OF BANBURY MODIFICATION AND MIXING WITH CARBON BLACK

[Variation Banbury Modification Time (35/15 MPC/HAF Black Stocks)]

| | 10* | 2 | 3 | 4 | 6 | 8 | 10 | 15 |
|---|---|---|---|---|---|---|---|---|
| | | | | Total mixing time—min./300° F | | | | |
| Stress-strain | | | | | | | | |
| M₃₀₀ (psi) | 1700 | 2100 | 2290 | 2170 | 2220 | 2030 | 2200 | 2170 |
| Torsional hysteresis | | | | | | | | |
| Logarithmic decrement @ 77° F | 0.412 | 0.203 | 0.176 | 0.185 | 0.174 | 0.150 | 0.178 | 0.177 |
| Goodrich flexometer | | | | | | | | |
| Dynamic drift, % | 17.9 | 15.4 | 13.8 | 14.9 | 13.9 | 13.0 | 13.0 | 14.0 |
| Permanent set, % | 20.4 | 15.5 | 16.0 | 16.3 | 14.8 | 15.6 | 15.8 | 15.9 |
| Heat rise, ° F | 47 | 43 | 36 | 38 | 36 | 34 | 36 | 36 |

* Blank control.

## TABLE VI

### EVALUATION OF ELASTOPAR IN FACTORY EQUIPMENT

|  | Laboratory | Factory | Factory* |
|---|---|---|---|
| Enjay Butyl 325 | 100.0 | 100.0 | 100.0 |
| Elastopar | 0.9 | — | 0.9 |
| MPC black | 40.0 | 40.0 | 40.0 |
| Necton (†) 60 | 8.0 | 8.0 | 8.0 |
| Stearic acid | 0.5 | 0.5 | 0.5 |
| Zinc oxide | 5.0 | 5.0 | 5.0 |
| Sulfur | 1.5 | 1.5 | 1.5 |
| Tellurac‡ | 1.0 | 1.0 | 1.0 |
| Thiofide | 1.0 | 1.0 | 1.0 |
| Cure 40'/307° F | | | |
| Stress-strain | | | |
| 300% modulus (psi) | 1190 | 800 | 1200 |
| Tensile strength (psi) | 2150 | 2140 | 2040 |
| Ultimate elongation (%) | 460 | 570 | 440 |
| Yerzley oscillograph | | | |
| 122° F, 16 cps | | | |
| Dynamic modulus (dynes/cm.²× 10⁻⁷) | 2.14 | 2.89 | 2.38 |
| Relative damping (%) | 32.3 | 40.0 | 3.11 |
| Internal viscosity (poises × 10⁻⁵) | 0.555 | 0.979 | 0.594 |
| Goodrich Flexometer | | | |
| Permanent set (%) | 11.0 | 23.0 | 15.3 |
| Dynamic drift (%) | 8.6 | 16.2 | 9.0 |
| Heat rise, ° F | 43 | 57 | 45 |

\* Conditions of Banbury mixing:
0 minute—Charge Butyl, carbon black, zinc oxide, stearic acid, and Elastopar to No. 11 Banbury @ 40 rpm.
7 minutes—Temp. 340° F. Add Necton 60.
10 minutes—Dump temp. 350° F.
† Necton—A registered trade mark of Esso Standard Oil Co. (Mineral oil).
‡ Tellurac—A trade mark of R.T. Vanderbilt Co. (Tellurium diethyl dithiocarbamate).

*Modification at various carbon black loadings.*—A commonly observed phenomenon in Butyl rubber and in other elastomers is an increase in hysteresis with carbon black loading. It is demonstrated in Figure 3 that this effect is much less for Banbury-mixed MPC/HAF stocks in the presence of Elastopar. The magnitude by which the modifier reduces hysteresis is directly proportional to concentration of carbon black. These results imply an interdependence between chemical modification and pigment reinforcement.

*Factory-scale evaluation.*—The work with the laboratory Banbury was extended to factory evaluation of chemical modification. A No. 11 Banbury was used under normal conditions of operation. Elastopar modifier was added to

## TABLE VII

### COMPARISON OF PROPERTIES OF HAF/MPC BLACK STOCKS FOR DIFFERENT REACTION METHODS

|  | Control | Elastopar* reacted with gum polymer | Elastopar* reacted with Butyl/carbon black mix |
|---|---|---|---|
| 300% modulus (psi) | 1460 | 2070 | 1900 |
| Tensile strength (psi) | 2820 | 2680 | 2760 |
| Elongation (%) | 510 | 410 | 450 |
| Logarithmic decrement @ 77° F | .398 | .159 | .228 |

\* Concentration: 1.5 parts/100 parts Butyl rubber.

## TABLE VIII

### EFFECTS OF REACTING ELASTOPAR WITH BUTYL/CARBON BLACK MIXES UNDER STATIC CONDITIONS IN AN OVEN

[Properties after Modification in Oven (HAF and MPC Black Stocks)]

| | Masterbatches | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Enjay Butyl 217 HAF black | | | | Enjay Butyl 217 MPC black | | | |
| Elastopar, phr | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | — | 0.3 | 0.9 | 1.5 | — | 0.3 | 0.9 | 1.5 |
| | | | | 100 50 | | | | 100 50 |
| Oven heating of masterbatch, hr./300°F | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| **Properties of vulcanizate** | | | | | | | | |
| $M_{100}$ (psi) | 1520 | 1910 | 1780 | 1720 | 900 | 1190 | 1290 | 1420 |
| $M_{200}$ (psi) | 1680 | 2000 | 2350 | 2440 | 1390 | 1470 | 1890 | 1840 |
| $M_{300}$ (psi) | 2580 | 2900 | 2620 | 2600 | 3170 | 3180 | 3220 | 3170 |
| Tensile (psi) | 2650 | 2830 | 3030 | 3040 | 3280 | 3170 | 3330 | 3250 |
| Elongation (%) | 490 | 460 | 400 | 410 | 700 | 670 | 630 | 620 |
| Torsional hysteresis (log. decr. @ 77°F) | 0.45 | 0.38 | 0.31 | 0.30 | 0.44 | 0.37 | 0.29 | 0.27 |
| | 0.41 | 0.28 | 0.18 | 0.16 | 0.37 | 0.26 | 0.17 | 0.15 |
| Mooney scorch | 13.7 | 13.5 | 12.7 | 12.7 | 13.4 | 13.6 | 13.8 | 12.5 |
| Min/275° F (1 + 10) | 16.6 | 17.3 | 19.8 | 19.8 | 17.5 | 17.5 | 17.0 | 18.3 |

NOTE: Addition of vulcanizing system and curing conditions are as described in Table I.

TABLE IX

300% MODULUS AND LOGARITHMIC DECREMENT VALUES—MODIFICATION
IN PRESENCE OF OTHER COMPOUNDING INGREDIENTS

Recipe:

| | |
|---|---|
| Enjay Butyl 217 | 100.0 |
| Elastopar | 1.5 |
| HAF black | 15.0 |
| MPC black | 35.0 |
| Zinc oxide | 5.0 |
| Stearic acid | 3.0 |
| Thiofide | 1.0 |
| Thiurad | 1.0 |
| Sulfur | 2.0 |

Heat treatment: 1' @ 300° F, 10-minute total cycle in Banbury mixer
Cure:              45'/307° F

| Additives present during heat treatment of Butyl rubber | Logarithmic decrement | |
|---|---|---|
| | $M_{300}$ | @ 77° F |
| Elastopar | 1950 | 0.203 |
| Elastopar, zinc oxide, stearic acid | 1860 | 0.201 |
| Elastopar, Thiofide | 1980 | 0.177 |
| Elastopar, Thiurad | 890 | 0.334 |
| Elastopar, Thiofide, Thiurad | 1240 | 0.267 |
| Elastopar, zinc oxide, stearic acid, Thiofide, Thiurad | | |
| Elastopar, sulfur | Scorched in the Banbury | |
| Elastopar, zinc oxide, stearic acid, sulfur | | |

the mixer simultaneously with Butyl rubber, carbon black, zinc oxide, and
stearic acid.    The recipe and procedure employed and the results derived are
shown in Table VI.    Laboratory evaluation of the same recipe is included for
comparison.

Good agreement was obtained between laboratory and factory processing.
The stress-strain data show a 1½-fold increase in 300% modulus for the factory
and laboratory stocks over the unmodified factory stock.    Dynamic modulus,
as measured by the modified Yerzley oscillograph[6], is reduced by more than
25 per cent in the laboratory run and 17.5 per cent in the factory test.    Similar
improvements are obtained in relative damping and internal viscosity.    Good-
rich flexometer data greatly favor modified Butyl rubber in both laboratory and
factory tests.

The factory data indicate that laboratory results may be duplicated on a
commercial scale and are a tribute to the effectiveness of the modifier at the
modest concentration of 0.9-part (0.3-part active ingredient).

*Order of addition of Elastopar and other ingredients.*—As an alternative to
incorporating the modifier into the raw Butyl polymer and subsequently heat
treating this system, it is also practicable to incorporate the additive into a
Butyl rubber-carbon black mixture and to react the system under either
dynamic or static conditions.    Table VII shows that substantial improvements
in modulus and torsional hysteresis are obtained under dynamic conditions in
the Banbury mixer by this order of mixing.    The results, particularly hyster-
esis, are not quite equal to those yielded by the modified-gum control stock,
but still represent large improvement.

Significant improvements in modulus and torsional hysteresis also are ob-

## TABLE X

### ELASTOPAR IN VARIOUS BUTYL RUBBER VULCANIZATION SYSTEMS

| Base stocks | | Min. cure @ 307° F | Normal control | Heat treated control | Heat-treated Elastopar-modified |
|---|---|---|---|---|---|
| Enjay Butyl 217 | | | 100 | 100 | 100 |
| HAF black | | | 15 | 15 | 15 |
| MPC black | | | 35 | 35 | 35 |
| Temperature of Banbury mixing, ° F | | | 212 | 300 | 300 |
| **1.** Sulfur | (2.0) | 60 | | | |
|    Thiofide | (1.0) | | | | |
|    Thiurad | (1.0) | | | | |
|    Modulus (300%) | | | 1500 | 1770 | 2290 |
|    Ultimate tensile strength | | | 2860 | 2900 | 2920 |
|    Elongation | | | 520 | 480 | 390 |
|    Torsional hysteresis (log. decr.) | | | .44 | .39 | .20 |
| **2.** Sulfur | (2.0) | 60 | | | |
|    Tellurac | (3.0) | | | | |
|    Modulus (300%) | | | 1930 | 2200 | 2580 |
|    Ultimate tensile strength | | | 2450 | 2700 | 2580 |
|    Elongation | | | 430 | 370 | 300 |
|    Torsional hysteresis (log. decr.) | | | .45 | .36 | .18 |
| **3.** Sulfur | (2.0) | 60 | | | |
|    Ethyl Selenac | (3.0) | | | | |
|    Modulus (300%) | | | 1850 | 2030 | 2550 |
|    Ultimate tensile strength | | | 2560 | 2580 | 2670 |
|    Elongation | | | 430 | 400 | 330 |
|    Torsional hysteresis (log. decr.) | | | .47 | .38 | .18 |
| **4.** Sulfur | (2.0) | 30 | | | |
|    GMF | (6.0) | | | | |
|    Red lead | (10.0) | | | | |
|    Modulus (300%) | | | 2400 | 2110 | 2220 |
|    Ultimate tensile strength | | | 2400 | 2360 | — |
|    Elongation | | | 300 | 350 | 290 |
|    Torsional hysteresis (log. decr.) | | | .32 | .28 | .20 |
| **5.** GMF | (6.0) | 30 | | | |
|    Red lead | (10.0) | | | | |
|    Modulus (300%) | | | 1710 | 1410 | 1570 |
|    Ultimate tensile strength | | | 2270 | 2210 | 2100 |
|    Elongation | | | 420 | 450 | 410 |
|    Torsional hysteresis (log. decr.) | | | .34 | .31 | .25 |
| **6.** Dibenzo GMF | (6.0) | 30 | | | |
|    Red lead | (10.0) | | | | |
|    Sulfur | (2.0) | | | | |
|    Modulus (300%) | | | 1730 | 1820 | 1880 |
|    Ultimate tensile strength | | | 2330 | 2285 | 2220 |
|    Elongation | | | 420 | 400 | 360 |
|    Torsional hysteresis (log. decr.) | | | .43 | .39 | .26 |
| **7.** Dibenzo GMF | (6.0) | 30 | | | |
|    Red lead | (10.0) | | | | |
|    Modulus (300%) | | | 1820 | 1930 | 1820 |
|    Ultimate tensile strength | | | 1930 | 1930 | — |
|    Elongation | | | 320 | 300 | 290 |
|    Torsional hysteresis (log. decr.) | | | .43 | .41 | .28 |
| **8.** Sulfur | (2.0) | 45 | | | |
|    Thiotax | (2.0) | | | | |
|    Thiurad | (1.0) | | | | |
|    Modulus (300%) | | | | 1550 | 2270 |
|    Ultimate tensile strength | | | | 2740 | 2720 |
|    Elongation | | | | 490 | 400 |
|    Torsional hysteresis (log. decr.) | | | | .38 | .17 |

TABLE XI

LOW–TEMPERATURE AND ELECTRICAL RESISTIVITY—NORMAL
vs. HEAT–TREATED BUTYL RUBBER STOCKS

|  | Normal control | Heat-treated control | Heat-treated elastopar modified |
|---|---|---|---|
| $T_{2000}$, ° F, Clash-Berg | +7.7 | +9.5 | −16.6 |
| Electrical resistivity, ohm-cm. | $2.7 \times 10^5$ | $3.9 \times 10^6$ | $4.9 \times 10^{14}$ |

tained when Elastopar is incorporated into Butyl rubber/carbon black mixtures and heated under static conditions in a 300° F oven.    These data are described in Table VIII.

Table IX summarizes an experiment involving chemical modification with Elastopar in the presence of other ingredients of the recipe.    No change in properties occurs as the result of incorporating zinc oxide plus stearic acid prior to chemical modification.    The presence of accelerators influences modulus and torsional hysteresis: Thiofide intensifies the effect of Elastopar; while Thiurad diminishes its activity.    The additions of sulfur, sulfur plus zinc oxide and stearic acid, or a combination of accelerators plus zinc oxide and stearic acid prior to the modification step cause a strong scorching effect during the Banbury operation and resultant impaired processability of the stocks.

It has also been found that processing oil can be added prior to chemical modification without incurring adverse effects.

*Elastopar in Butyl vulcanizing systems.*—The data in Table X show that the benefits which Elastopar modifier imparts to Butyl rubber extend in significant degree to all the main types of vulcanizing systems which are conventionally used with Butyl rubber.    The GMF[9] and Dibenzo GMF[10] systems respond less vigorously to the action of Elastopar than do systems based upon Thiofide/Thiurad, Thiotax[11]/Thiurad, Tellurac, and Ethyl Selenac[12].

*Electrical resistivity and low-temperature properties after modification.*—Significant changes which are obtained in the low-temperature properties and electrical resistivity of Butyl rubber as a result of chemical modification by Elastopar are shown in Table XI.    The $T_{2000}$, that temperature where torsional
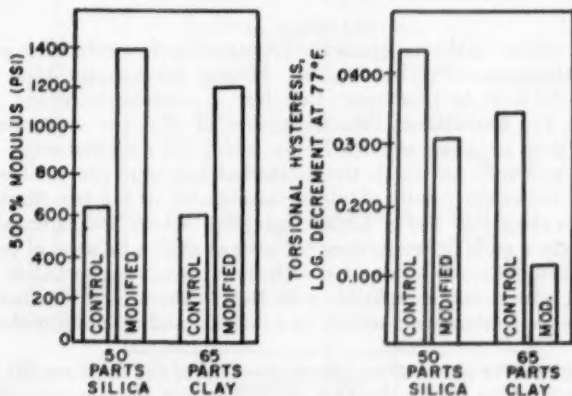


FIG. 4.—Effects of chemical modification in silica and clay stocks.

modulus is 2000 psi, is lowered by 24° F. The striking increase in electrical resistivity, from $10^6$ to $10^{14}$ ohm-cm., signifies much improved dispersion of carbon black in the Butyl rubber polymer.

*Silica- and Clay-reinforced stock modification.*—Gessler and Rehner[5] have shown that improvements in modulus and resilience of silica-reinforced Butyl rubber vulcanizates are realized through heating a Butyl/silica system in the presence of Dibenzo GMF. Figure 4 shows the effects of using Elastopar-modified Butyl rubber in silica- and clay-loaded stocks. The formulations and mixing conditions for these stocks are listed in Table XII. The 500% moduli are doubled, and torsional hysteresis values are markedly decreased with the use of modified Butyl rubber.

*Elastopar masterbatches.*—Since the new modifier is effective at low dosages, its use in the masterbatched form may be desired. In view of the predicted high reactivity of Elastopar with the Butyl rubber molecule, the advisability of

TABLE XII

RECIPES AND MIXING CONDITIONS FOR CLAY AND SILICA STOCKS

I. Mix on rubber mill @ 122° F

Base A

| | |
|---|---|
| Enjay Butyl 217 | 100.0 |
| Elastopar | 1.5 |

II. Heat treatment in air oven, 4 hours/212° F

III. Compound on rubber mill @ 122° F

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Enjay Butyl 217 | 100 | — | 100 | — |
| Base A | — | 100 | — | 100 |
| Hi-Sil* 233 | 50 | 50 | — | — |
| Suprex Clay† | — | — | 65 | 65 |
| Stearic acid | 2 | 2 | 1 | 1 |
| Glycerol | 3 | 3 | — | — |
| Zinc oxide | 5 | 5 | 5 | 5 |
| Ethyl Tellurac | 1 | 1 | 1 | 1 |
| Sulfur | 2 | 2 | 2 | 2 |

IV. Cure 45'/307° F

* Hi-Sil—A registered trade mark o ' Pittsburgh Plate Glass Co., Pittsburgh, Pa.
† Suprex Clay—A registered trade m ark of J. M. Huber Corp., New York.

using Butyl rubber as the matrix in the preparation of masterbatch was thought to be questionable. Polyisobutylene, having no unsaturation, would be expected to be inert to Elastopar; therefore, a commercial grade, Vistanex[13], was chosen for evaluation. Masterbatches of 37.5 per cent concentration of modifier were prepared in both Enjay Butyl 217 and Vistanex. Temperature of the mill rolls on which the masterbatches were prepared was 122° F. Table XIII shows the results obtained through use of the two masterbatches.

The data show that use of Enjay Butyl 217, which has an unsaturation of approximately 2 mole per cent, does not give as good a balance of properties as are obtained from the stock prepared with the Vistanex masterbatch. Vistanex is, of course, completely compatible with Butyl rubber, and the small quantity added to the recipe should act merely as a softener and extender without adverse effect.

*Other evidence for chemical modification.*—One of the most readily recognized of the distinguishing properties of a vulcanizate of Elastopar-modified Butyl rubber is a sensation of improved resilience and snap when the cured stock is

TABLE XIII

ELASTOPAR MASTERBATCHES

I. Preparation of masterbatches on
mill at 122° F

| | A | B |
|---|---|---|
| Enjay Butyl 217 | 62.5 | — |
| Vistanex | — | 62.5 |
| Elastopar | 37.5 | 37.5 |

II. Heat treatment in Banbury, pro-
cedure in Table I

| | 1 | 2 | 3 |
|---|---|---|---|
| Enjay Butyl 217 | 100.0 | 100.0 | 100.0 |
| Elastopar | 1.5 | — | — |
| A | — | 4.0 | — |
| B | — | — | 4.0 |
| MPC black | 35.0 | 35.0 | 35.0 |
| HAF black | 15.0 | 15.0 | 15.0 |

III. Final compounding

| | | | |
|---|---|---|---|
| Zinc oxide | 5.0 | 5.0 | 5.0 |
| Thiofide | 1.0 | 1.0 | 1.0 |
| Thiurad | 1.0 | 1.0 | 1.0 |
| Sulfur | 2.0 | 2.0 | 2.0 |

IV. Cure 45′/307° F

| | | | |
|---|---|---|---|
| 300 Modulus (psi) | 2000 | 1580 | 1880 |
| Ultimate tensile strength (psi) | 2710 | 2770 | 2600 |
| Elongation (%) | 440 | 500 | 430 |
| Torsional hysteresis (log. decr.) | 0.182 | 0.289 | 0.205 |

flexed manually.   The leathery quality of the control stock contrasts sharply with the greater ease of deformation and quicker and more nearly complete return upon release of the modified stock.

Three observations have been made which point very strongly to the exist-ence of a chemical reaction of Butyl rubber with the modifier.   A sample of
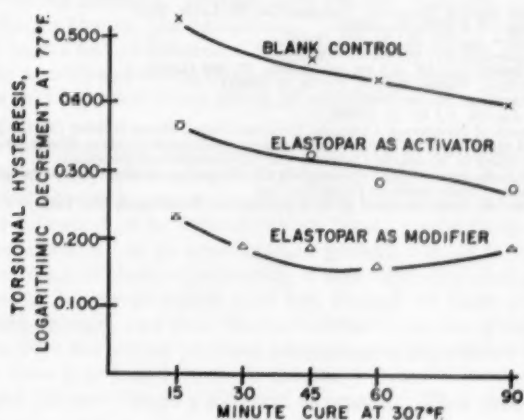


FIG. 5.—Function of Elastopar as vulcanization activator versus modifier.

Elastopar-modified Butyl rubber has been shelf-aged eight months and exhibits none of the cold flow which characterizes conventional Butyl rubber. A condition of reduced surface tack also has been observed. Ultraviolet spectrophotometric analysis has shown that there are no significant residual quantities of unchanged modifier following the chemical modification step.

Figure 5 summarizes torsional hysteresis comparisons of control and Elastopar-modified stocks versus one in which the modifier was incorporated as an activator for the vulcanizing system. The activated stock parallels the work of Trepagnier[14], in which he showed that N-methyl-N,4-dinitrosoaniline was an effective activator for Butyl rubber. The data reveal that a much different effect is obtained when Elastopar functions as a chemical modifier than when it is present as an activator in the final mix. The gum polymer contains no benzene-insoluble material after modification.

## SUMMARY

A new approach is presented toward obtaining improved properties in Butyl rubber vulcanizates through chemical modification of the Butyl rubber polymer by N-methyl-N,4-dinitrosoaniline. Chemical modification by this additive may be carried out in a Banbury mixer at conventional mixing times and temperatures. The use of modified polymer is advantageous in both black- and non-black-loaded stocks and is advantageous also with respect to variation over the spectrum of vulcanizing systems which are normally used with Butyl rubber. A successful plant demonstration of chemical modification has been carried out.

## ACKNOWLEDGMENTS

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[10] Dibenzo GMF—A trade mark of Naugatuck Chemical (p-Quinone dioxime, dibenzoate).
[11] Thiotax—A trade mark of Monsanto Chemical Co. (2-Mercaptobenzothiazole).
[12] Ethyl Selenac—A trade mark of R. T. Vanderbilt Co. (Selenium diethyldithiocarbamate).
[13] Vistanex—A registered trade mark of Enjay Co., Inc.
[14] US 2,457,331 (Dec. 28, 1948), assigned to E. I. du Pont de Nemours & Co., Inc.

# CHEMICAL ASPECTS OF REINFORCEMENT *

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The problem of how carbon black is able to reinforce rubber vulcanizates is still controversial. Some workers believe that the mechanism is at least partly chemical, whereas others claim that it is entirely physical in nature. The aim of the work described here is to determine the extent of the contribution to reinforcement of chemical interaction between the carbon black and the rubber vulcanizate.

It is generally agreed that the reinforcing ability of carbon black usually increases with its specific surface. A notable exception to this rule occurs when medium processing channel (MPC) and high abrasion furnace (HAF) blacks are compared. The HAF blacks, which have the lower specific surface (as measured by the electron microscope) impart greater abrasion resistance to natural rubber vulcanizates than do the MPC blacks. Another exception occurs when the MPC black Spheron 6 is compared with its graphitized form, Graphon. The abrasion resistance imparted to natural rubber vulcanizates by Graphon is only 70 per cent of that imparted by Spheron 6[1], although both carbon blacks have the same specific surface, as measured by the electron microscope. These facts suggest that the reinforcing action is not entirely physical in nature.

From a study of the effect of prestressing on vulcanizates loaded with various fillers, Blanchard and Parkinson[2] distinguished two types of linkage between the filler and the rubber. One type is present with all fillers and such linkages are termed "weak linkages" because they can be ruptured by prestressing the rubber. The other type is present only with carbon black and these are termed "strong linkages" because they are not ruptured by prestressing. Using Blanchard's theory, the exceptional behavior of HAF blacks compared with channel blacks and of Spheron 6 compared with Graphon can be explained in terms of the numbers of strong linkages formed with the rubber. This theory also indicates that the reinforcing action of carbon black is not entirely physical in nature.

Smith and his coworkers[3] once thought that certain chemisorbed complexes on the surface of fully reinforcing carbon blacks might react chemically with the unsaturated groups known to be present in the rubber molecule. To test this idea they adsorbed on to various carbon blacks model compounds such as dihydromyrcene which has an unsaturation pattern similar to that of natural rubber. As a result of these experiments, it was concluded that the reinforcing ability of carbon blacks probably does not depend on their ability to react chemically with rubber[2], and that the exceptional behavior of fully reinforcing blacks results from the strong physical adsorption of the rubber by the sites of high activity that they found on these blacks.

Stearns and Johnson[4] made a different approach. They measured the heat

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of adsorption of bromine by Graphon and by several fully reinforcing carbon blacks. They claimed that the fully reinforcing blacks had unsaturated groups on their surface. With Graphon, no such groups could be found. As a result of this, Stearns and Johnson suggested that fully reinforcing carbon black could be linked chemically through sulfur to the rubber by a process analogous to ordinary vulcanization. Thus, in their view, the superior reinforcing ability of Spheron 6 over Graphon arose because the rubber was chemically linked to the Spheron 6 but not the Graphon.

Parkinson and the author[5] reported work in which a channel black was brominated and hydrogenated. Such treatments would be expected to eliminate all unsaturated groups on the surface of the carbon black, yet in each case the reinforcing ability of the black remained unaltered. These facts contradicted the theory of Stearns and Johnson and showed that unsaturation of the surface of the channel black does not contribute to its reinforcing ability.

Watson and his colleagues showed that milling can cause rupture of rubber molecules into free radicals. Convincing evidence was furnished[6] to show that some of these radicals can react chemically with carbon black to form a cross-linked network. Their theory explains why, when rubber is milled with carbon black, some of the rubber is rendered insoluble in organic solvents such as benzene, i.e., bound rubber is formed. Watson concluded mainly from modulus changes that the ability of carbon black to accept free radicals during milling might be at least partly responsible for reinforcement[7]. Independent evidence in support of this theory has been reported by Garten and Sutherland[8] who showed that carbon black could accept free radicals from solution.

More recently Garten and Weiss[9] have presented evidence which indicates that part of the chemisorbed oxygen on reinforcing carbon blacks is present in the form of semiquinones. They claimed that the presence of these groups, which are known to be free radical acceptors, is responsible for the superior reinforcing ability of carbon blacks over other fillers. A serious objection to their view is that although the complete removal of oxygen from a channel black by heating it to 1250° C reduces modulus, it does not appreciably alter its reinforcing ability. This fact has been confirmed by a great number of road wear tests[10]. The term reinforcement used in this connection and throughout this paper, refers to the filler's ability to improve the abrasion resistance, tear resistance and tensile strength of the vulcanizates. Modulus is not regarded as a property of reinforcement.

From these considerations of previous work it seemed probable that milling carbon black with rubber could cause the rubber to be chemically crosslinked by the black by a free radical mechanism. The important question, which was then still unanswered, was "To what extent does such a mechanism influence reinforcement?" The first approach used to answer this question directly was to try to saturate all the free radical acceptor sites on a fully reinforcing carbon black by reacting the black with excess free radicals before mixing it with rubber. If chemical reaction between the rubber free radicals and the black were a factor in reinforcement then this elimination of acceptor sites should cause a reduction in the black's reinforcing ability.

## INFLUENCE OF FREE RADICAL TREATMENT ON REINFORCING ABILITY OF CARBON BLACK

Garten and Sutherland[8] claimed that sulfate free radicals, produced by heating aqueous potassium persulfate solution, react chemically with rein-

forcing carbon blacks. It was decided to use their method because of its simplicity and because only simple inorganic byproducts are formed.

## EXPERIMENTAL

500 g. quantities of the fully reinforcing carbon blacks Philblack O and Spheron 6 were heated for 2 days at 80° C with 500 g. of potassium persulfate dissolved in 5 liters of water. The residual persulfate was then destroyed by boiling the mixture for 1 hour.

The persulfate ion decomposes in hot aqueous solution according to the following equations:—

$$S_2O_8^{--} \rightleftharpoons SO_4^- \cdot + SO_4^- \cdot \tag{1}$$

$$SO_4^- \cdot + H_2O \rightarrow HSO_4^- + OH \cdot \tag{2}$$

$$OH \cdot + OH \cdot \rightarrow H_2O_2 \tag{3}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4}$$
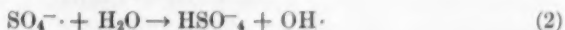
Thus the net effect of decomposing potassium persulfate is that the acid salt potassium hydrogen sulfate and oxygen are formed.

$$2H_2O + 2K_2S_2O_8 \rightarrow 4KHSO_4 + O_2 \tag{5}$$

It was essential that all the free acid generated should afterwards be removed before the black was mixed with the rubber to avoid upsetting the vulcanization system. Attempts were made to wash out the acid by repeated dilution and centrifuging, but it was found that when the salt concentration was reduced below a certain limit, colloidal dispersion of the black took place. To avoid this difficulty a sample was removed as soon as dispersion began, and the acid completely washed out using dilute potassium chloride solution to prevent dispersion. From an analysis of the washings the quantity of alkali to be added to the bulk sample to neutralize the acid was calculated. The water around the black was then removed by evaporation. The samples so prepared contained about 3 per cent by weight of potassium sulfate.

To correct for any effects on the reinforcing ability of the blacks resulting from the presence of the salt or from the method of introducing it, blank samples of the blacks containing identical quantities of salt were prepared. To do this, a quantity of aqueous sulfuric acid, equivalent to that produced by the persulfate treatment was added to the blacks, and then neutralized with alkali. Finally, the quantity of salt thus formed on the blacks was adjusted by washing to be the same as that on the persulfate treated samples.

## DISCUSSION

According to Garten and Sutherland[8] the decomposition of potassium persulfate in the presence of carbon black leads to chemisorption of the sulfate free radicals, formed as intermediates, Equation (1), and the black (Cb) thereby acquired a negative charge

$$Cb \cdot + SO_4^- \cdot \rightarrow Cb \ SO_4^- \tag{6}$$

This mechanism readily explains the remarkably increased dispersibility of carbon blacks in aqueous solution after such treatment.

Precipitation tests using polyvalent ions revealed that the treated carbon blacks, when dispersed in aqueous solution, were negatively charged in agreement with the mechanism proposed by Garten and Sutherland. However, ultimate analysis of the treated blacks washed free from acid by the potassium chloride could detect no increase in their sulfur content; this contradicted the theory of Garten and Sutherland, and revealed that no chemisorption of sulfate free radicals had taken place. On the other hand, there was a definite increase in the amount of chemisorbed oxygen on both carbon blacks. The most likely explanation of this increase in oxygen content is that hydroxyl free radicals formed by exchange between the sulfate free radicals and the water, Equation (2), were chemisorbed by the black.

$$Cb \cdot + OH \cdot \rightarrow CbOH \qquad (7)$$

This mechanism does not readily explain why the carbon blacks become negatively charged by the treatment. A possible explanation is that the introduction of oxygen on to the black causes some of the hydrogen atoms on the surface to become acidic and therefore able to dissociate from the black as ions leaving it negatively charged

$$CbOH \rightleftharpoons CbO^- + H^+ \qquad (8)$$
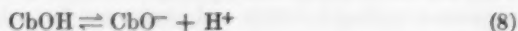
The persulfate treated blacks were compared at optimum cure in natural rubber at 50 parts loading both with the corresponding blank samples and with samples of the original untreated carbons. In each case the persulfate treatment caused a marked reduction in reinforcing ability of the blacks (Table I). Comparison of the data for the blank samples with those for the original blacks showed only a small decrease in properties. Thus the fall in properties was mainly due to the persulfate treatment.

Measurements using the B.E.T. low temperature nitrogen adsorption method[11] showed no significant difference between the specific surfaces of the persulfate treated Philblack O and the corresponding blank sample (Table I). Consequently the reduced reinforcing ability of the treated black indicated that active sites on the surface of the black had been eliminated. The addition of the 3 per cent of potassium sulfate to form the blank sample reduced the specific surface by about 6 per cent (Table I), which is greater than would be expected on a weight basis. This shows that the salt can effectively seal off some of the surface of the carbon presumably by blocking spaces between the

TABLE I

INFLUENCE OF POTASSIUM PERSULFATE TREATMENT ON
REINFORCING ABILITY OF CARBON BLACK

| Type of black | Tensile strength, kg./cm.² | Modulus at 300% | Abrasion | Tear strength | Bound rubber | Swelling index | Specific surface, M²/gm. |
|---|---|---|---|---|---|---|---|
| Original Philblack O | 205 | 152 | 109 | 26 | 74 | 18 | 80 |
| Philblack O Blank sample | 202 | 144 | 99 | 27 | 75 | 19 | 75 |
| Persulfate treated Philblack O | 166 | 109 | 80 | 19 | 71 | 17 | 76 |
| Original Spheron 6 | 254 | 119 | 87 | 39 | — | — | 132 |
| Spheron 6 Blank sample | 244 | 120 | 83 | 39 | — | — | 121 |
| Persulfate treated Spheron 6 | 201 | 98 | 62 | 27 | — | — | 101 |
| Graphon Blank sample | 198 | 35 | 71 | 32 | 64 | 25 | 93 |
| Persulfate treated Graphon | 217 | 50 | 69 | 34 | 96 | 24 | 100 |

particles or by covering surface pores. With Spheron 6, the specific surface of the persulfate treated black was lower than that of the blank sample (Table I). This is believed to be due to the salt in the treated black being distributed in such a way so as to seal off more internal surface. Whatever the cause of this difference, as it is difficult to see how the chemical treatment could have caused a significant increase in its particle size, it is considered highly probable that the external specific surfaces (i.e., the surface available to the rubber) of the persulfate treated Spheron 6 was not less than that of the blank sample. Accordingly, the fall in reinforcing ability (Table I) caused by the persulfate treatment indicated that active sites on the surface of the black had been eliminated.

In the case of Spheron 6 the treatment reduced the abrasion resistance by about 30 per cent which is the same as the reduction when the black is graphitized to form Graphon. It is possible therefore that both the potassium persulphate treatment and graphitization eliminate all the chemically active sites on Spheron 6 contributing to reinforcement. If this were the case, the reinforcing action left after such treatments might be entirely physical in nature.

To test this idea the potassium persulfate treatment was applied to Graphon. In contrast to the behavior of Spheron 6 and Philblack O, when the treated Graphon was washed free from the potassium bisulfate (Equation 5), colloidal dispersion did not take place. Ultimate analysis revealed a definite increase in the oxygen content of Graphon, though the increase was smaller than that for Spheron 6 and Philblack O. Surface area measurements showed that this treatment had slightly increased the black's specific surface, presumably because the oxidation had etched the surface to some extent (Table I).

Comparison of the treated and the blank Graphon in natural rubber at 50 parts loading showed that the persulfate treatment had not appreciably altered the reinforcing ability of Graphon (Table I). This supports the view that graphitization had removed all the chemically active sites which contribute to reinforcement, and so there were none to be removed by the persulfate treatment. On the other hand, the treatment did increase modulus. It is interesting to compare this large increase in modulus without change in reinforcing properties to what happens when channel blacks are furnace treated to remove chemisorbed oxygen. When Spheron 4 is heated to 1250° C the modulus is reduced yet the abrasion resistance, tensile strength and tear resistance remain substantially unchanged[10]. It would appear, therefore, that the small quantity of oxygen introduced on the Graphon by the persulfate treatment caused the modulus increase. Whatever the detailed mechanism of the modulus changes induced by the chemical or furnace treatment, it will be clear that a considerable part of the stiffness imparted to rubber vulcahizates by carbon black results from a specific reactivity of the surface which does not influence the carbon black's reinforcing ability.

It is because of facts such as this that it is not sufficient, when testing reinforcement theories, to show that a proposed mechanism explains modulus changes. It is necessary to go further and relate the mechanism to reinforcement properties such as abrasion resistance, tear resistance and tensile strength.

The physical test data given in Table I are from three separate compounding experiments, one for each of the three types of carbon black employed. To minimize errors, which are always relatively large in abrasion testing, comparison should be confined to a single experiment. Thus the fact already mentioned that Graphon has 70 per cent of the abrasion resistance of Spheron 6 was not

calculated from the data in Table I, but from a separate compounding experiment in which these carbon blacks were compared directly[1].

Smith of the Cabot Carbon Co[12], found that treatment of a reinforcing black with sodium hypochlorite solution also caused a remarkable increase in its dispersibility in water, and suggested this might have the same effect on reinforcement as the persulfate treatment. To see if this were the case, the influence of sodium hypochlorite treatment on the reinforcing ability of Philblack O was investigated.

## EXPERIMENTAL

2.5 liters of 15 per cent w/v aqueous sodium hypochlorite were added to 600 g. of the black and allowed to react for 24 hours. Most of the residual sodium hypochlorite was then destroyed by boiling the mixture for an hour. As much as possible of the remaining salts were removed by repeated washing and centrifuging. The black could not be freed completely from salts by this procedure because, as with potassium persulfate, the black dispersed when the salt concentration was reduced below a certain limit. As a result of this the black so prepared contained about 3 per cent by weight of sodium chloride. This quantity of sodium chloride was determined by washing a sample of the black free from chloride with dilute potassium sulfate solution. Analysis of these washings, using acidified potassium iodide, showed the treated black to be free from hypochlorite and chlorate.

## DISCUSSION

The hypochlorite treated Philblack O was compared in natural rubber at 50 parts loading with a blank sample which also contained 3 per cent by weight of sodium chloride. The hypochlorite treatment caused a marked reduction in the reinforcing ability of the black (Table II), the extent of the decrease being roughly similar to that produced by potassium persulfate. Comparison of the data for the blank sample with that for the original black showed only a small decrease in properties. Therefore the fall in properties was mainly caused by the hypochlorite treatment.

Further tests showed that the effects of the sodium hypochlorite treatment on Philblack O were in every way similar to those produced by the potassium persulfate. Thus low temperature nitrogen adsorption showed no appreciable change in specific surface (Table II) and there was an increase in oxygen content. Also the treated Philblack O was found to be negatively charged in aqueous solution. The similarity of the effect of both the treatments made it seem likely that a similar mechanism was operating in each case.

Of the several possible ways in which the hypochlorite ion $OCl^-$ could have reacted with the carbon black, the following two are the most probable from the standpoint of the energies involved. The ion could have added on to un-

TABLE II

INFLUENCE OF SODIUM HYPOCHLORITE TREATMENT ON
REINFORCING ABILITY OF CARBON BLACK

| Type of black | Tensile strength, kg./cm.$^2$ | Modulus at 300% | Abrasion | Tear strength | Bound rubber | Swelling index | Specific surface, M$^2$/gm. |
|---|---|---|---|---|---|---|---|
| Original Philblack O | 225 | 148 | 98 | 32 | 80 | 19 | 74 |
| Philblack O Blank sample | 219 | 135 | 88 | 30 | — | — | 67 |
| Hypochlorite treated Philblack O | 171 | 88 | 63 | 13 | 81 | 18 | 65 |

saturated groups on the surface of the black by an ionic mechanism, e.g.,

$$\underset{\diagdown C \diagup}{\overset{\diagup C \diagdown}{\underset{\|}{}}} + OCl^- \longrightarrow \underset{\diagdown C-Cl^+ \diagup}{\overset{\diagup C \diagdown}{\underset{|}{}}} + O^- \longrightarrow \underset{\diagdown C\ Cl \diagup}{\overset{\diagup CO^- \diagdown}{}}$$
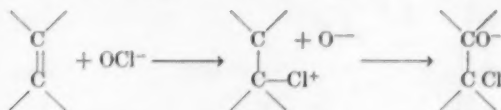
This possibility must be rejected because no chemisorption of chlorine took place. Alternatively the ion could have split into chlorine free radicals and oxygen radical ions $Cl\cdot$ and $O\cdot^-$ which would form hydroxyl free radicals by exchange with the water, i.e., $O\cdot^- + H_2O \rightleftharpoons OH^- + OH\cdot$ and $Cl\cdot + H_2O \rightleftharpoons OH\cdot + H^+ Cl^-$.

The hydroxyl free radicals so formed could then react with the black. Such a mechanism is identical with that proposed to account for the potassium persulfate treatment, Equations (7) and (8), and would explain why the two different treatments had the same effect on the blacks. Independent evidence in support of this free radical interpretation is the fact that aqueous sodium hypochlorite solution can initiate polymerization as recently reported by Cooper of Dunlop Research Center[12], and by Kern[14] in a review of work in Germany. It is thought, therefore, that all the facts concerning both the sodium hypochlorite and the potassium persulfate treatments can be most reasonably explained by supposing that free radical attack of the blacks took place. In the light of this interpretation the decrease in properties caused by the treatments indicates that the reinforcing ability of carbon black partly results from a free radical interaction between the black and rubber. However, the evidence presented so far does not indicate at what stage this particular free radical mechanism took place. In view of the work of Watson[6,7] it seemed likely at this point in the investigation that the free radical mechanism in question occurred during milling. According to this theory both the formation and swelling behavior of bound rubber are a direct consequence of free radical interaction between the rubber and the black during milling. It appeared, therefore, that a fair test of this theory would be to see how far bound rubber and its swelling index were related to reinforcement.

## RELATIONSHIP OF BOUND RUBBER AND SWELLING INDEX TO REINFORCING ABILITY OF CARBON BLACK

### EXPERIMENTAL

Fifteen different carbon blacks including Graphon were selected which covered the full particle size range used in rubber compounding and which included examples of all the principal types. With the blacks Seval, Philblack A, Philblack O, Vulcan 6, Vulcan 9, Lampblack, P33, Sterling L, Sterling 99, Sterling S, Sterling V and Graphon the recipe used was rubber 100, sulfur 2.5, Santocure 0.5, stearic acid 2.0, zinc oxide 5.0 and carbon black 50.0. With the blacks Spheron N, Spheron 6 and acetylene, Santocure and sulfur were increased to 0.8 and 2.8, respectively. Pale crepe was used because it was found that smoked sheet contained appreciable quantities of polymer gel which would have been reckoned as bound rubber. All the mixes were prepared from a sample of pale crepe which had previously been rendered homogeneous by mastication as a single batch.

Bound rubber determinations were carried out on separately prepared rubber-filler samples, free from all vulcanization ingredients, by standing 0.25 g.
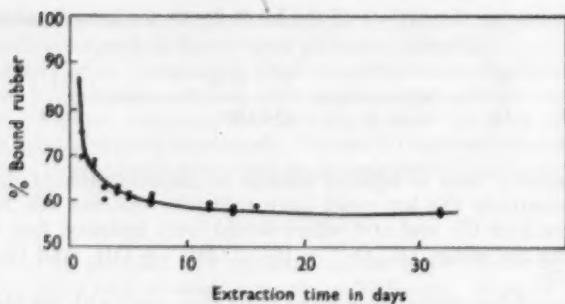
Fig. 1.

of the samples in 100 ml. of benzene for 7 days at 25° C.   The benzene in the insoluble rubber black residue was then removed by oven drying at 80° C. Bound rubber is expressed as the percentage of insoluble rubber per unit weight of black.   The reproducibility of the data was about ±2 per cent.   Systematic variation of the extraction time showed (Figure 1) that after 7 days the bound rubber decreased only very slowly.   It was concluded from this that extraction was complete after 7 days and that the slow decrease after that time was because of oxidation.   This interpretation has been confirmed by the recent work of Angier and Watson[15] who showed that errors due to oxidation during 7 days at 25° C are small.

To carry out swelling index measurements the swollen insoluble rubber-carbon residues were freed from excess benzene by dipping successively in petroleum ether and diethyl ether.   The residual diethyl ether was then easily removed by evaporation in a stream of air.   Finally, the swollen gel was weighed and the quantity of benzene it contained calculated.   Swelling index is expressed as the weight of benzene held per unit weight of insoluble rubber. The reproducibility of the swelling index data was about ± 3 per cent.   The rubber-filler mixes prepared using the two blacks having the lowest specific surface—P33 and Seval—partially dispersed in benzene.   These two blacks were not tested further.

Abrasion resistance was measured using the Dunlop Constant Power Lambourn machine[16].

### DISCUSSION

The abrasion resistance for the remaining thirteen carbon blacks was plotted against their specific surface as measured by the electron microscope.   The electron microscope specific surface values were used because they are a measure of the external surface of the carbon black particles.   The values determined by nitrogen adsorption are frequently higher than those determined by the microscope because of the internal surface from pores in the particles.   It is considered unlikely that appreciable quantities of rubber could penetrate inside any pores that exist in carbon black.

With the exception of the special blacks, acetylene and Graphon, the correlation between abrasion resistance and specific surface is quite good (Figure 2), the data being scattered about a curve.   Closer inspection, however, shows that the curve can be regarded as an upper and lower curve corresponding to blacks prepared from oil and gas, respectively.   Thus the "oil" furnace blacks,

Abrasion resistance (y-axis, 40 to 120)

PHIL. O.
V. 6   V. 9
S.N
PHIL. A.
S. 6
ST. V.
ST. 99
ST. L   •ACET.   •G
ST. S.
•L.B.

E. M. Specific surface M²/gm.
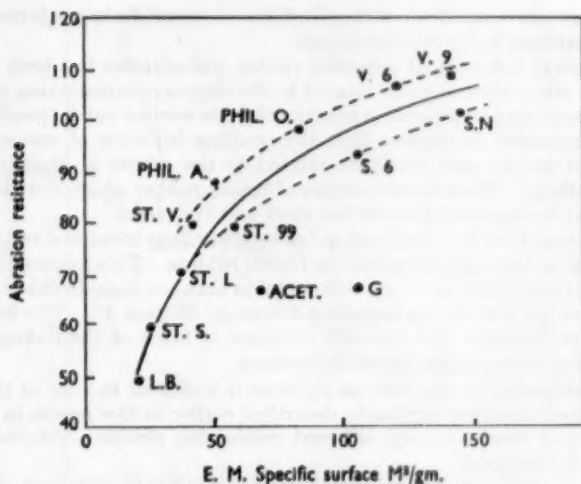
Fig. 2.

Sterling V, Philblack A, Philblack O, Vulcan 6 and Vulcan 9 all fall on the upper curve. Whereas, the "gas" blacks Sterling S, Sterling L, Sterling 99, Spheron 6 and Spheron N all fall on the lower curve. This difference has been observed repeatedly and is therefore probably significant.

These facts suggest that all the blacks in a given family have the same reactivity per unit area of surface and that the reactivity per unit area of the "oil" blacks is higher than that of the "gas" blacks. By the same reasoning, the special blacks acetylene and Graphon are regarded as belonging to families having reactivities per unit area which are even lower than that of the "gas" blacks. If the reactivity per unit area of a black corresponds to its ability to accept rubber free radicals during milling and thereby form bound rubber, we would expect those blacks with the highest reactivity to form the most bound rubber per unit area.

Figure 3 shows the bound rubber values for the thirteen blacks plotted against specific surface. With the exception of Graphon (G) the correlation between bound rubber and specific surface is good and, as other workers have found, the points are scattered about a straight line. Those blacks which had the greatest reactivity had no tendency to form more bound rubber than the average black. Further, if Graphon is neglected, those blacks which had the least reactivity had no tendency to form less bound rubber than the average black. It seems, therefore, that bound rubber is no better related to reinforcing ability than is specific surface.

In the case of the special black Graphon, the bound rubber per unit specific surface was much lower than that for any of the other blacks, and therefore in line with its abnormally low reinforcing ability. It could be argued that bound rubber is not determined sufficiently precisely by the number of chemical linkages formed between the rubber and the black for it to distinguish adequately between the "oil" and "gas" blacks which after all do not differ greatly in reinforcing ability. By this view, the behavior of Graphon could be regarded as

showing that the number of rubber-to-filler chemical linkages formed during milling is responsible for reinforcement.

The swelling behavior of unloaded rubber vulcanizates has been shown by Flory[17] and other workers to be related to the degree of crosslinking of the rubber. Although no corresponding theory has been worked out for loaded rubber, it seems reasonable to suppose that the swelling behavior of uncured carbon black-loaded rubber also would be related to the extent of crosslinking produced by milling. Thus those samples of bound rubber which were least crosslinked would be expected to swell the most and vice versa.

It was found that the relationship between swelling index and reinforcement was identical to that just described for bound rubber. This followed inevitably from the fact that there was a good correlation between bound rubber and swelling index for all the blacks including Graphon (Figure 4). The behavior of Graphon was therefore still the only evidence in favor of the linkages formed during milling being related to reinforcement.

The relationship of Graphon to Spheron 6 is similar to that of the treated to the untreated reinforcing blacks described earlier in this paper, in that they are all pairs of blacks having different reinforcing abilities, yet identical external specific surfaces.

As has already been shown both chemical treatments decreased all the reinforcing properties, yet there was no significant change in either bound rubber or swelling index (Tables I and II). Even modulus, which also decreases, was not related to bound rubber or swelling index. In the case of Graphon the per-
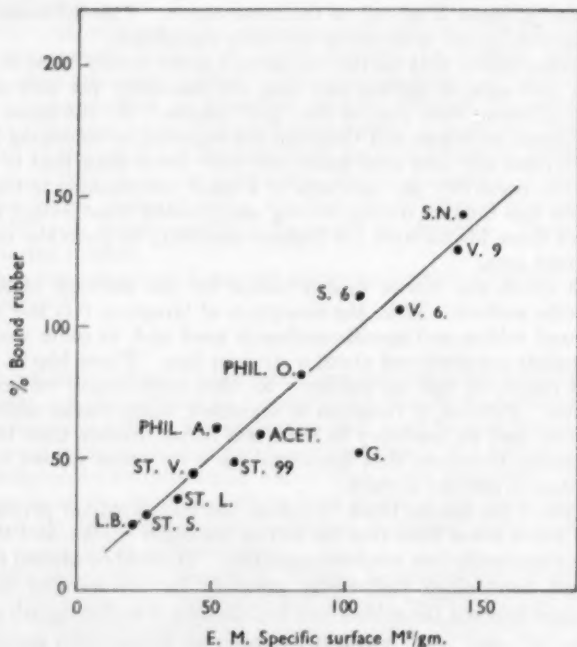


Fig. 3.
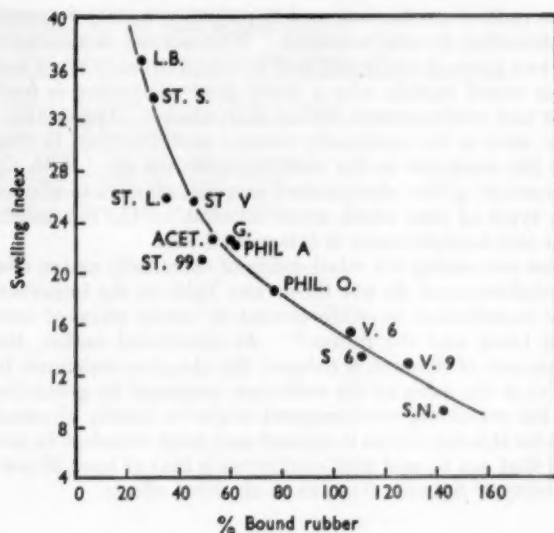
Fig. 4.

sulfate treatment did not alter its reinforcing ability, though it did increase modulus.   Thus the increase in bound rubber (Table I) was in line with modulus but not with reinforcing ability.   With swelling index, which did not change appreciably, the converse was the case.

It will be clear from all these comparisons that neither bound rubber nor swelling index is uniquely related to the reinforcing ability of carbon black.   If we accept the very reasonable view put forward by W. F. Watson that the extent of the free radical interaction that occurs during milling is related to the swelling behavior and quantity of bound rubber formed, then we must also conclude that this free radical interaction is not uniquely related to reinforcement. On the other hand, the evidence from the chemically treated blacks did suggest that a free radical mechanism was responsible for at least some reinforcing ability of carbon blacks.   A mechanism which reconciles these facts is to suppose that the particular free radical reaction principally responsible for reinforcement takes place mainly during vulcanization.   W. F. Watson[7] came to a similar conclusion with regard to the modulus changes produced by carbon blacks.   The most direct evidence in support of this theory is the data for the potassium persulfate and sodium hypochlorite treated Philblack O, the reinforcing ability of the black was reduced, yet neither the swelling index nor quantity of bound rubber changed.   These facts strongly suggest that the treatments did not alter the interaction between the blacks and the rubber during milling, but in some way altered the black's influence on the rubber during vulcanization.

The evidence presented in this paper taken in conjunction with that furnished by W. F. Watson suggests that at least two different types of active sites exist on the surface of reinforcing carbon blacks.   One type can react with rubber free radicals formed during milling and may not be a factor in reinforcement.   The other type can react with rubber during vulcanization, perhaps

also by a free radical mechanism, and is probably mainly responsible for the chemical contribution to reinforcement. With normal commercial blacks the extent of the two types of site might well be related to each other and to specific surface. This would explain why a fairly good correlation is found between bound rubber and reinforcement among such blacks. Apparently, only when special blacks, such as the chemically treated ones described in this paper, are considered is the weakness in the correlation shown up. With Graphon the complete removal of all the chemisorbed material appears to eliminate at least some of both types of sites which would account for the relationship between bound rubber and reinforcement in this special case.

These ideas concerning the relationship of chemically active sites to bound rubber and reinforcement do not throw any light on the important question, "What is the contribution to reinforcement of purely physical interaction between carbon black and the rubber?" As mentioned earlier, the fact that chemical treatment of Spheron 6 reduced the abrasion resistance by about 30 per cent, which is the same as the reduction produced by graphitization, does suggest that the remaining reinforcement might be largely physical in nature. The evidence for this conclusion is indirect and must therefore be accepted with caution. All that can be said with confidence is that at least 30 per cent of the reinforcing ability of Spheron 6 is due to chemical effects.

## SUMMARY

Hydroxyl free radicals were chemisorbed on to the surface of fully reinforcing carbon blacks by reacting them with an aqueous solution of potassium persulfate or of sodium hypochlorite. Both treatments caused a marked decrease in reinforcing ability, from which it was concluded that free radical interaction between these carbon blacks and rubber is a factor in reinforcement.

Bound rubber and swelling index, which were determined for commercial carbon blacks covering the full range of particle size used in rubber compounding, were found to be no better related to reinforcing ability than was specific surface. In addition, after hydroxyl free radical treatment, bound rubber and swelling index remained unaltered though the reinforcing ability had been reduced. It was concluded, therefore, that the free radical interaction between carbon black and rubber which contributes to reinforcement occurs mainly during vulcanization, not during milling.

## ACKNOWLEDGMENTS

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# ASPECTS OF THE PHYSICAL BASIS OF REINFORCEMENT *

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## INTRODUCTION

The suitability of a rubber for most applications is usually determined by its physical and mechanical properties, of which the three most important are stiffness, strength and abrasion resistance. An understanding of these properties and of their measurement in relation to specific service conditions is fundamental in any assessment of the quality or suitability of rubbers. This paper describes some of the results of recent investigations at the BRPRA concerned with developing this understanding with particular reference to the "reinforcement" of rubber vulcanizates.

## STIFFNESS

One of the first characteristics considered in the technological evaluation of rubber vulcanizates is stiffness, and traditionally an increase of stiffness has often been associated with reinforcement. Increases in stiffness can be produced in a variety of ways, for example, by the addition of any filler, by compounding with resins, by modification of the chemical structure of the rubber, or merely by increase in the degree of crosslinking. The resultant materials, though stiff, differ considerably in overall quality. Further, much of the stiffening effect of fillers is often readily destroyed by deforming the rubber.

It appears that fillers produce a thixotropic structure within the rubber which breaks down during deformation, although much of the stiffness then lost may be recovered subsequently during standing. Figure 1 shows a typical family of tensile stress-strain curves obtained on a tire tread vulcanizate before and after deformation to various extensions[1,2]. The amount of structure which can be broken in this way depends upon the nature of the filler and rubber and upon the thoroughness of dispersion. The exact nature of this structure and its influence on stiffness remains obscure, but it is clear that the increase of stiffness is not the real source of improved quality which results from the addition of reinforcing fillers. Any attempt to describe the effect of fillers on the stiffness of rubber must take this thixotropic phenomenon into account. In the measurement of the stiffness of a filler-reinforced rubber, any of a wide range of values may be obtained depending upon the history of the rubber and the conditions of test. The usefulness of the results, however, is determined by how well these conditions line up with working conditions. As a result, routine measurements of the modulus of a reinforced vulcanizate are of limited practical value for design purposes in the use of the rubber for engineering applications.
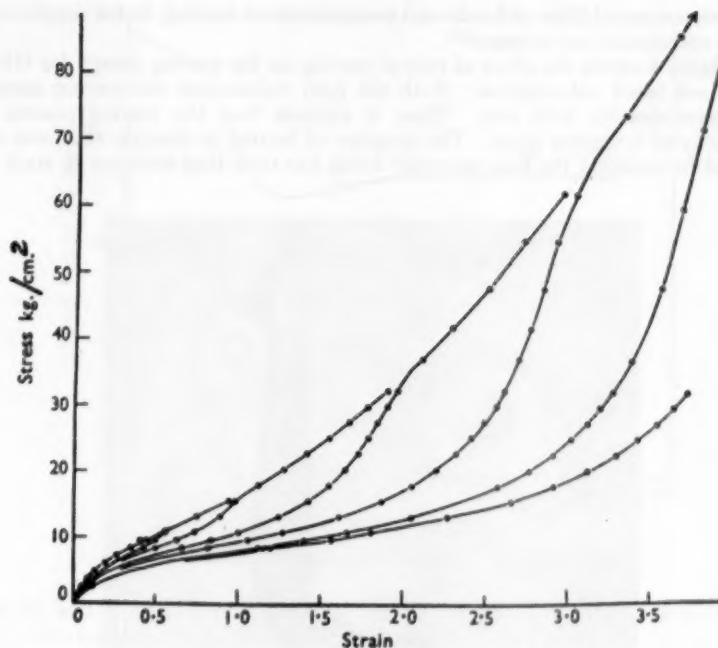
FIG. 1.—Stress-strain curves for tread vulcanizate.

However, an important aspect of the increase in stiffness produced by reinforcing fillers is that it reflects an ability to form a filler-structure and there is evidence from recent work on tearing and abrasion that readiness to form such a structure is an important characteristic in the development of strong tear and abrasion resistant vulcanizates.

## TEAR RESISTANCE

The rupture of rubber under stress or its cracking due to flexing or cyclic deformation is obviously influenced by its resistance to the growth of tears. It is well known that tear resistance is a difficult quality to standardize and measure objectively, and that conventional tests will often classify rubbers quite differently. The major advances made recently have been in developing rational ideas of what tearing means physically and in devising definitive methods of observing and measuring tear behavior.

In the first place it has been found possible to describe the tear quality of rubber in terms of a characteristic tearing energy[3]. This energy is related to the elastic energy stored in the highly strained zone at the tip of a growing tear. As the tear grows, most of this energy is dissipated irreversibly as heat, it being many times larger than that required to form the new surfaces[4]. A simple method for measuring this tearing energy has been worked out[2], and a "trousers" shaped test-piece shown in Figure 2 has been adopted as a preferred type. It is found that the value of the tearing energy is greatly influenced by the type of

rubber, nature of filler and rate and temperature of tearing, but a simple uni-
fying correlation has emerged[5,6].

Figure 3 shows the effect of rate of tearing on the tearing energy for GR-S
gum and tread vulcanizates. With the gum vulcanizate the tearing energy
increases steadily with rate. Thus, it appears that the tearing process is
basically of a viscous type. The progress of tearing is smooth, the force re-
quired to maintain the tear generally being less than that required to start it.



FIG. 2.—"Trousers" tear testpiece.

A different picture emerges with a tread vulcanizate. Here the addition of
reinforcing carbon black results in a very large increase in strength at low rates
of tearing. The tearing is knotty and shows stick-slip behavior. The tear
proceeds only for a short distance before it is stopped by a knot and then the
applied force has to build up before tearing continues. This knotty tearing is
due to the formation of a tear resistant structure at the tip of the growing tear.
At low rates of tearing sufficient time is given for this structure to form, but
at high rates the tear is propagated so quickly that it has insufficient time
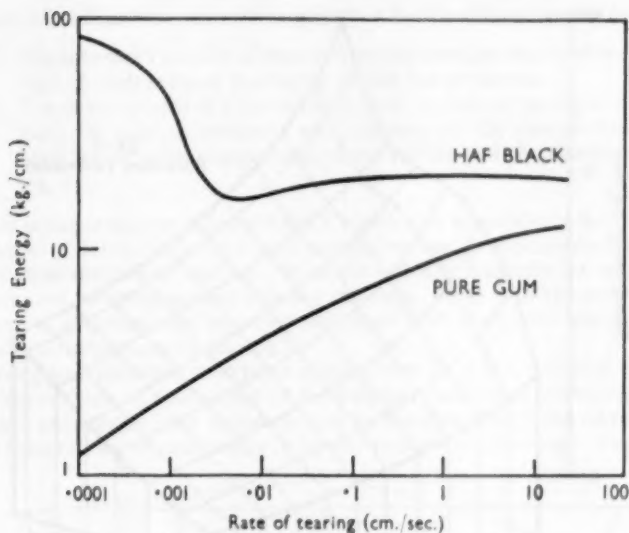
Fig. 3.—Effect of rate of tearing on strength of GR-S vulcanizates.

to form and the tear behavior of the tread vulcanizate reverts to that of the gum vulcanizate.

Figure 4 shows comparable data obtained on natural rubber vulcanizates. Here knotty or stick-slip tearing occurs with both gum and tread materials.
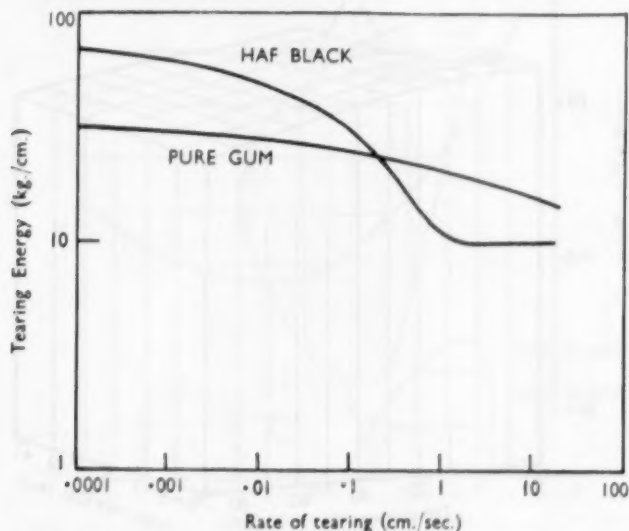


Fig. 4.—Effect of rate of tearing on strength of natural rubber vulcanizates.
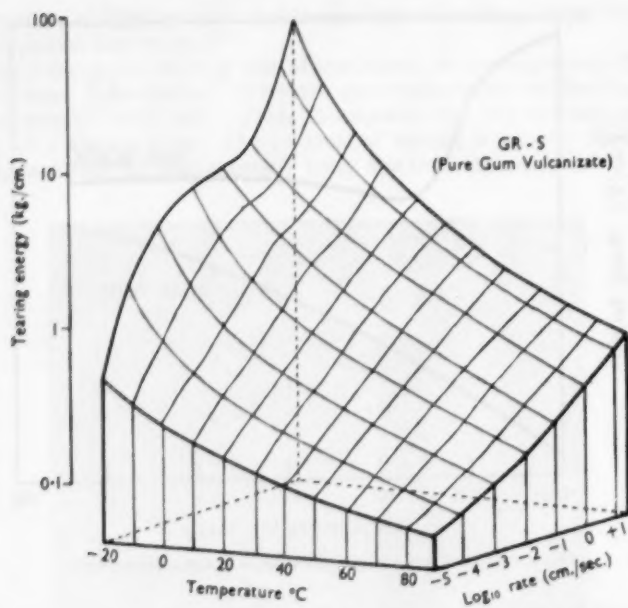
Fig. 5.—Tear behavior of GR-S gum vulcanizate.
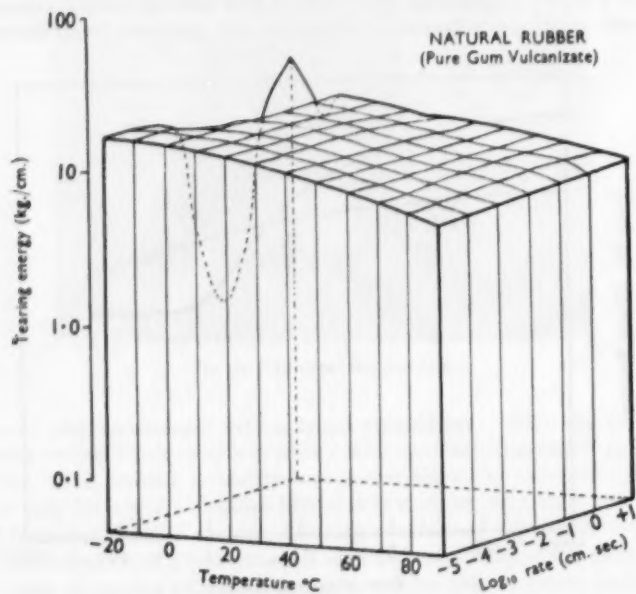


Fig. 6.—Tear behavior of natural rubber gum vulcanizate.

It appears that tear strength is governed by the following two factors:

(i) The internal viscosity of the rubber; the strength due to this cause being high at high rates of tearing or at low temperatures.
(ii) The development of a special structural change at the tip of the growing tear; the rate of formation and intensity of this change depends upon both the detailed composition of the rubber and the conditions of tearing.

This is illustrated by Figures 5 and 6 which give respectively the dependence of the tear resistance of GR-S and natural rubber gum vulcanizates on both temperature and rate of tearing. With the GR-S vulcanizate the tear behavior is dominated by the apparent internal viscosity, while with the natural rubber vulcanizate a strong tear resistant structure is formed over a wide range of rates and temperatures of tearing.

Strong tear resistant structures result either from the presence of reinforcing fillers or from crystallization of the polymer, both lead to the development of a hard anisotropic zone perpendicular to the direction of the advancing tear which forms a barrier and results in knotty or stick-slip tearing. An important
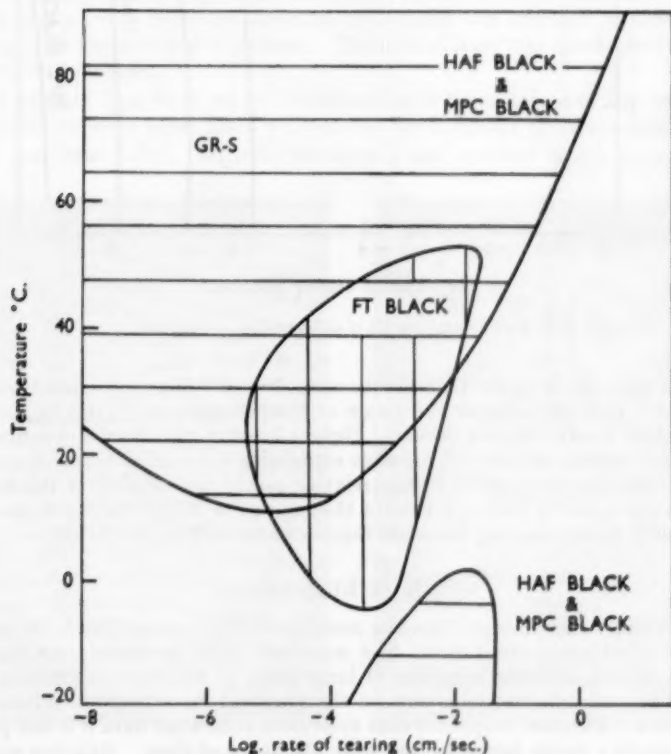


Fig. 7.—"Knotty" tearing of GR-S vulcanizates.
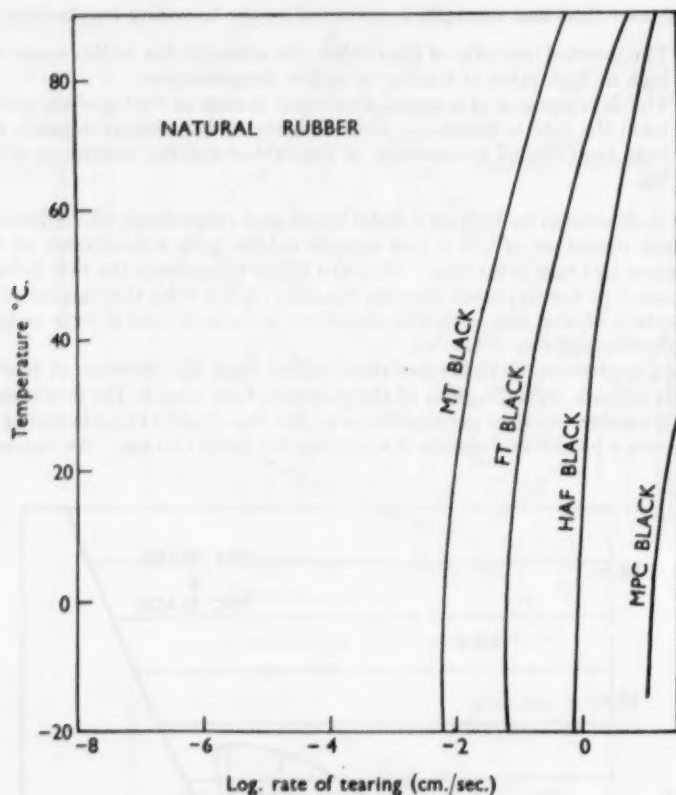
Fig. 8.—"Knotty" tearing of natural rubber vulcanizates.

means of characterizing the tear quality of reinforced vulcanizates now becomes apparent. It is to discover the range of temperatures and rates of tearing under which knotty tearing occurs. Figures 7 and 8 give results obtained on GR-S and natural rubber vulcanizates containing a range of types of carbon black which provide a guide to the relative reinforcing quality of the fillers. The shaded areas in Figure 7 denote the regions in which tearing is knotty. In Figure 8 knotty tearing occurs in regions to the left of the curves.

## ABRASION RESISTANCE

An even greater problem than the measurement of tear quality is the measurement of abrasion resistance. The standard methods provide notoriously arbitarary data, and the necessity of large fleets of test cars to evaluate the wear of tires is sufficient comment on the practical inadequacy of laboratory assessment. Further, it appears that even from road wear data it is not possible to obtain a single figure for the wear resistance of tires. Relative ratings depend upon the relative contributions of a number of factors such as roughness

of road, speed and severity of tests, temperature, and whether the road is wet or dry.

Recent investigations have provided a clue to some of the physical consequences of these several factors. The two photographs in Figure 9 show the surface of a typical tire tread mix abraded under laboratory conditions on rough and smooth concrete roads[7]. The ridges on the surface of the rubber are characteristic signs of an abrasion process, and these "abrasion patterns" are always at right angles to the direction of abrasion and lead to increased wear[8]. This increase is due to wear involving the bodily removal of relatively large particles of rubber from the crests of ridges in the pattern. When the patterns are pronounced the particles torn off in this way are large but when fine the particles are correspondingly smaller. The abrasion patterns are coarser the rougher the track or the softer the rubber. In the case of the samples shown in Figure 9 the rate of wear on the rough concrete road was about four times greater than that on the smooth road.

Results of an experiment demonstrating the importance of abrasion patterns in wear is shown in Figure 10. This gives the loss of weight of a flat sample which was abraded on a plane track. The conditions of abrasion for both of the curves in the figure were identical except that in the upper curve the direction of abrasion was always in the same sense and an abrasion pattern developed, while in the lower curve the direction of abrasion was changed periodically to prevent the formation of a pattern. The rate of wear was much greater when a pattern developed.

It appears that wear can be considered to be the outcome of two processes, one in which wear takes place without the development of an obvious pattern (this has been called "intrinsic abrasion") and another which involves the
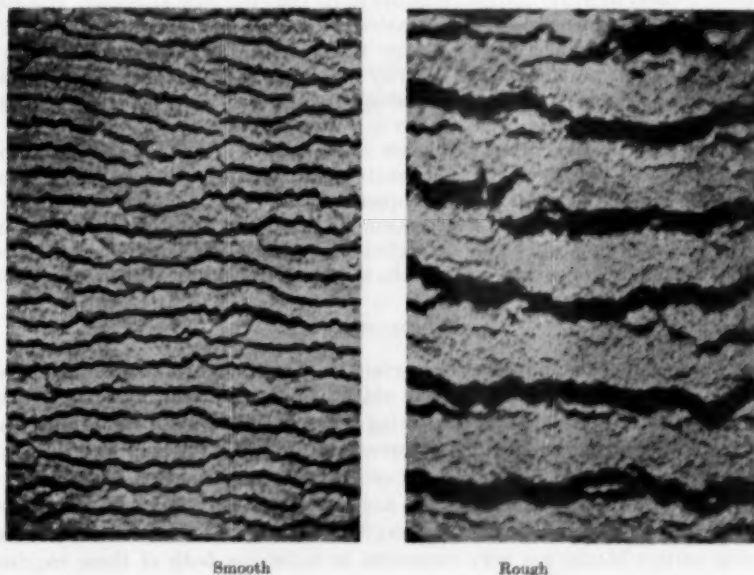


Smooth                                   Rough

Fig. 9.—Abrasion patterns developed on smooth and rough concrete roads.
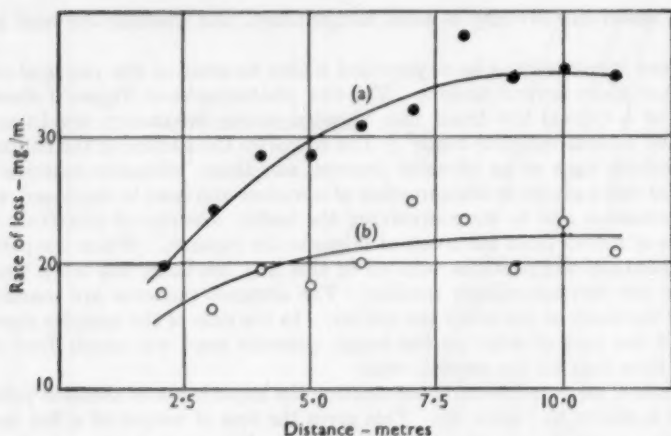
FIG. 10.—Effect of abrasion pattern on rate of wear. (a) with abrasion pattern. (b) without abrasion pattern.

development of a pattern[9]. The relative contribution of these two processes to overall wear depends upon the severity of conditions of abrasion. For example, under mild conditions of abrasion, measurements of "intrinsic abrasion" alone are appropriate for determination of relative wear ratings, but under more severe conditions these measurements have to be increasingly weighted with measurements of the facility with which an abrasion pattern is formed and of its contribution to wear. Measurements of (i) the "intrinsic abrasion" and (ii) the propensity to form an abrasion pattern, thus provide a possibility of forecasting the relative behavior of rubber under conditions of known severity. The appropriate measure of the severity of a wear experiment or a road trial may be simply determined from measurements of these two properties together with the wear ratings.

Model experiments carried out a few years ago[10] in a study of the nature of abrasion showed that local stress concentrations, produced mainly by friction, resulted in surface damage and subsequently in the detachment of small particles of rubber and thus drew attention to the important role of tearing in abrasive wear. It is thus to be expected that abrasion resistance will also be similarly strongly dependent on both the temperature and the rate at which the rubber is torn off.

## DISCUSSION

It appears that an important characteristic of rubber vulcanizates with good tear and abrasion resistance is their ability to form strong anisotropic tear resistant structures at the tips of growing tears, and is thus an important feature determining the quality of reinforced vulcanizates. A high level of reinforcement is associated with the rapid and substantial formation of such structures. In most applications it is also necessary that the rubber should not be so hysteretic that large amounts of energy are dissipated during its use. Reinforcing carbon blacks are very successful in satisfying both of these requirements. They are sufficiently fine to agglomerate and form strong chainlike

structures and, in addition, wet the rubber sufficiently to avoid any tearing away.

The use of measurements of stiffness, Wiegands' Δ A function, bound rubber or carbon gel as means of assessing reinforcement can now be reconsidered. Enhancement of any of these properties is not sufficient to indicate reinforcement, but they all have one feature in common, that is, they are all strongly sensitive to the formation of filler structure, and thus reflect a characteristic which, it is claimed, plays a very important role in the production of good tear and abrasion resistant rubbers.

## SUMMARY

Recent developments in rational ideas of what "reinforcement" means physically are described.   It is shown that probably the most important characteristic of rubber vulcanizates with good tear and abrasion resistance is their ability to form strong hard tear resistant structures at the tips of growing tears. The significance of this conclusion in relation to the assessment of the quality of rubber vulcanizates is discussed.

## ACKNOWLEDGMENT

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# ALUMINUM BLOCK HEATER FOR AGING RUBBER AND RUBBER COMPOUNDS AT HIGH TEMPERATURES *

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Rubber compounds are consistently being artificially aged at higher and higher temperatures. Much of the demand for aging at high temperatures is brought about by efforts to produce rubber compounds for the Air Force that will withstand temperatures of 400° to 550° F sometimes in contact with synthetic lubricants and hydraulic fluids. At these temperatures the usual circulating-air oven is difficult to control and often introduces a potential fire hazard, especially when rubber samples are immersed in organic fluids.

The purpose of this article is to describe the construction and operation of an aluminum block heater which has been found satisfactory for the aging of rubber compounds at these higher-than-usual aging temperatures. The same equipment, with adjustment in heater capacity, has operated quite satisfactorily at temperatures from just above ambient to 800° F.

The use of a circular aluminum block, fitted with electrical heaters and drilled to hold test tubes for aging rubber, has been described by Blum, Shelton and Winn and the B. F. Goodrich Chemical Co[1]. The first aluminum block heaters constructed by the authors adapted the Goodrich data to a rectangular aluminum block so that a larger number of samples could be aged. A smaller circular aluminum block heater has since been commercialized[2].

So far as is known, each of these heater designs has given very satisfactory service. A large part of their excellent performance has probably been due to the stabilizing effect of the aluminum mass and heat capacity on temperature control. This article, however, will describe only the rectangular aluminum block design.

*Design and construction details.*—The details for the fabrication of a rectangular aluminum block heater are presented in Figures 1 to 5; while the actual materials required are tabulated in Table I. A section of an aluminum ingot was obtained, which, when machined, was approximately 18 by 36 by 10 inches. Since the ingot as received had somewhat curved sides and shrink holes, the original size, about 19 by 36 by 10 inches, was machined to obtain level sides for the mounting of strip heaters. While other shapes of aluminum can be utilized, these are often formed only by special casting or forging operations, which greatly increase the cost of the aluminum.

This size of ingot section can be drilled with holes to contain as many as 60 test tubes having a diameter of 38 millimeters (about 1.5 inches). This number of holes does not impair the uniform conduction of heat to all parts of the block from the electrical strip heaters placed on the sides of the block. Test tubes placed at various locations in the block all read the same temperature, provided empty holes were corked to prevent local cooling.

The machined and drilled aluminum block, fitted with strip heaters, was placed on a low heavy-duty dolly in an insulated cabinet.    Firebricks were used as supports for the aluminum block, as both strength and insulation were desired for this support.    The cabinet was fitted with high-temperature insula-
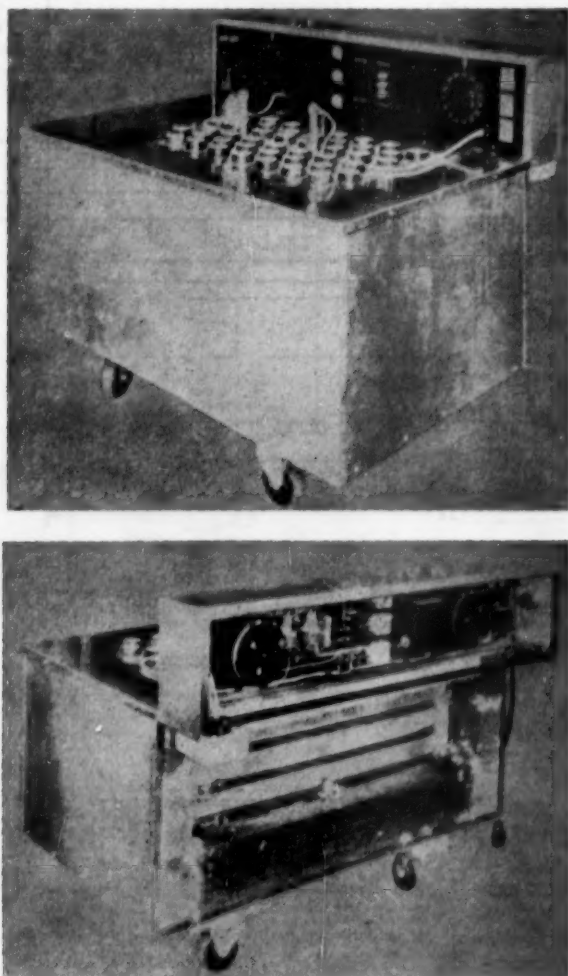


Fig. 1.—Front view (left) and rear view (above) of aluminum block heater for aging of rubber and rubber compounds.

tion and equipped with electrical controls that maintained a regulated uniform temperature.

While the relatively inexpensive controls selected were totally adequate and found to be reliable for continuous service for more than two years, many other
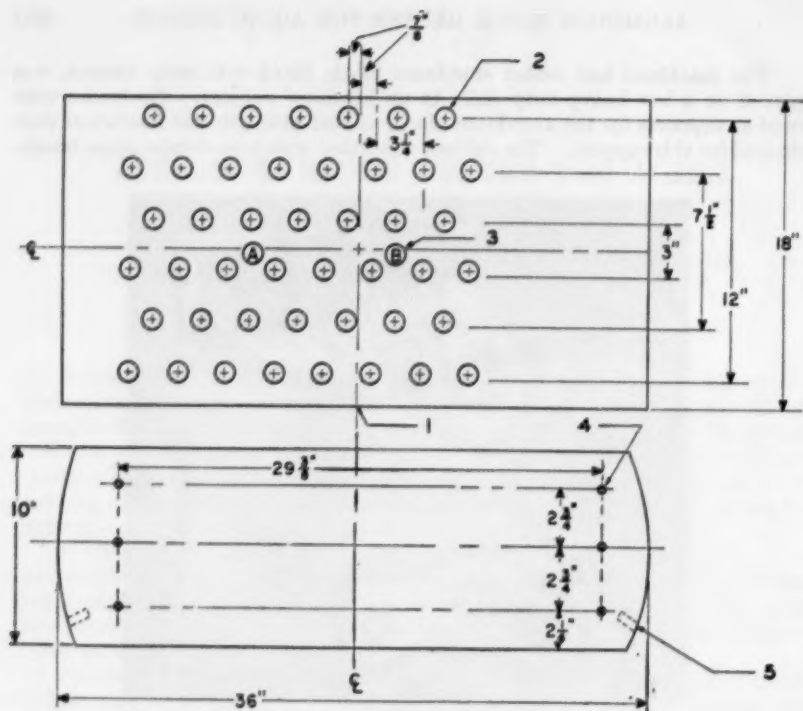
Fig. 2.—Machining specifications for aluminum block: (1) Lay out block from center line as shown. (2) Drill 60 holes, 1 1/8 inches in diameter and 7 inches deep overall with spacing as shown (45 holes only in above diagram because space at left reserved for hole of different dimension). (3) A, B, thermoregulator holes, 1/2-inch in diameter by 7 inches deep. Locate in the center of the two three-hole patterns as shown. (4) No. 7 drill, 1 1/2 inches deep, tap, 1/4—20NC—1, 6 holes, two sides, for mounting strip heaters. (5) Drill lifting pinholes, two per end; size depends on lifting device that is used.
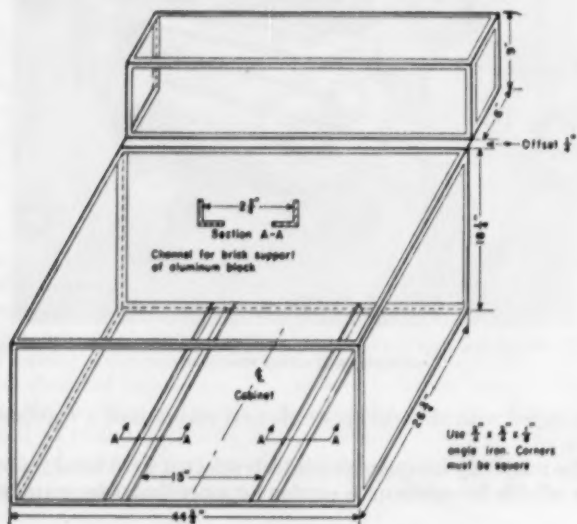


Fig. 3.—Diagram of cabinet frame for heating block.

FIG. 4.—Details of control panel for aluminum block heater.



FIG. 5.—Wiring diagram for aluminum block heaters.

## TABLE I

### PARTS LIST AND SPECIFICATIONS FOR ALUMINUM-BLOCK HEATER

| Item | Part | Specification | Source* |
|------|------|---------------|---------|
| 1 | Aluminum block | As-cast ingot, 10 by 36 by 19 inches Alloy 28 Machining details given in Figure 3 | Aluminum Co. of America |
| 2 | Aluminum tubing | 1¼- by 0.058-inch— Type 618 | ———— |
| 3 | Cabinet frame | ¾- by ¾- by ⅛-inch angle iron Frame details given in Figure 4 | ———— |
| 4 | Cabinet | Sheet aluminum | ———— |
| 5 | Insulation | B. H. Monoblock, 36 by 6 by 4 inches | Baldwin-Hill, Trenton, N. J. |

* Where items and sources are not specified, any general supplier of the desired equipment should be able to furnish the necessary part. Materials used in the construction of this unit are not necessarily recommended over other comparable materials that can perform the same function.

TABLE I—*Continued*

| Item | Part | Specification | Source* |
|------|------|---------------|---------|
| 6 | Strip heaters | 4—Type SN-3045 strip heaters, 230 volts, 450 watts, Monel sheath<br>2—Type SNH-30 strip heaters, 230 volts, 1000 watts, Monel sheath | E. L. Wiegand Co., Pittsburgh, Pa. |
| 7 | Temperature controllers | 2—No. 13150 Fenwal controllers<br>Modifications:<br>(1) Length of temperature sensitive shell, 11 inches to flange<br>(2) Lead wire, 28 inches<br>(3) Armored cable, 28 inches | Fenwal, Inc., Ashland, Mass. |
| 8 | Variacs | 2—Type V10H | General Radio Co., Cambridge, Mass. |
| 9 | Transformer | 100 volt - amperes, Catalog No. 710-21, 230 volts to 115 volts G-E | ——— |
| 10 | Relays | 2—Mercury relays, Catalog No. 7020, 110-volt coil, 30 amperes | H. B. Instrument Co., Philadelphia, Pa. |
| 11 | Resistors | 4—1 watt, 4700 ohms<br>2—40 ohms | H. B. Instrument Co., Philadelphia, Pa. |
| 12 | Condensers | 2—0.005 microfarad | ——— |
| 13 | Control jacks | 2—Cinch-Jones plugs No. P 302CCT<br>2—Cinch-Jones sockets No. S-302-FP | ——— |
| 14 | Selector switches | 3—Cutler-Hammer Model C-2 DPDT 30 amperes, 125 volts, alternating current | ——— |

CAUTION: The Fenwall controllers specified for these blocks are tension operated and should not be inserted in a hot block without first setting the Fenwal to the approximate block temperature. Conversely, a Fenwal in a heated block should not be reset for a temperature lower than 200° F below the block temperature. In either case, the stress induced may damage the controller.

controls could be adapted to this general design. The advantages that might be offered by a more elaborate and expensive control system, however, are of doubtful value, except when extremely small temperature variations are demanded.

*Controls.*—The control system employed was designed with a view to provide (1) a continuous supply of heat to the block that was just short of the desired temperature, (2) an intermittent supply of heat that would be slightly in excess of that needed to attain the desired temperature, (3) a temperature regulator that would shut off the intermittent heater when the desired tempera-

### TABLE II

#### FUNCTION OF CONTROL-PANEL COMPONENTS—FIGURE 4

| Component | Function |
|---|---|
| Master switch | This is a double-pole single throw switch that disconnects both legs of the 230-volt supply. |
| Main indicator light | This light glows when power is on. Power failure or a burned-out instrument fuse or main fuse will prevent lighting. |
| Temperature-indicator | This indicates block temperature relative to control-temperature setting of the Fenwal regulator. Light burns when the block temperature is low and controller is calling for heat. Circuit will not supply heat, however, unless heater switch, center of panel, is on and selector switch is set for heat. |
| Instrument fuse | This is a low-amperage instrument fuse used as protection in the transformer circuit. Failure turns out all indicating lights. |
| Master plug-type fuse | This is a 20-ampere fuse used to protect against overload or major short in the unit. Failure cuts all indicating lights. |
| Left Variac | This is wired to govern the input voltage to the top pair of heaters. This set of heaters is controlled manually and is continuous when it is in operation. |
| Heater fuses | Fuse protection is provided for each set of heaters, i.e., top, center, and bottom. The plug fuses are oriented in the same relative position as the heater sets protected. Failure of a fuse will turn off the corresponding indicator light. |
| Heater-circuit switches | On-off switches are provided for each set of heaters and are positioned like the set controlled, i.e., top, center, and bottom. |
| Heater-circuit indicators | An indicator light is provided for each heater circuit. Failure of the light when the switch is on and the fuse intact indicates the power has been cut off by the safety Fenwal controller. If all lights are out, points listed under (B) should be checked. |
| Right Variac | This governs the input voltage to the center (Fenwal controlled) pair of heaters. |

TABLE II—*Continued*

| Component | Function |
|---|---|
| Heat-selector switches | A selector switch is provided for each pair of heaters, i.e., top, center, and bottom. Orientation of the switch is the same as that of the heater set controlled. Each selector switch has three positions: |

    (1) toggle up—high heat
    (2) toggle center—no heat
    (3) toggle down—low heat

Note: It is advisable to switch off either the main power or the heater-circuit power before changing the selector switch. Heater circuit indicator lights are not controlled by the selector switches. Lights may be burning, therefore, without heat going to the block if the selector switches are in the "off" position.

ture was attained, and (4) a second temperature regulator to control all heat input in the event of an excessive overheat.

The two Variacs were installed in the system as a means of adjusting the heat input of the continuous and intermittent heaters, which comprise the top two pairs of heaters. The lower pair of heaters, controlled only by selector switches, were available for supplying additional heat. The setting of the Variacs, to a large extent, determined the temperature variance obtained. With a little experience, temperatures were maintained with $\pm 2°$ F for operating temperatures of 350–550° F. At 800° F the variation was about $\pm 5°$ F.

The arrangement of the electrical components is shown in Figures 4 and 5. Instructions for operating the control panel are presented in Table II. In the actual wiring of this system, it is highly desirable to make connections to the heaters with wire that is heat resistant, as ordinary copper wire will crystallize, and its insulation will burn off.

## SUMMARY

A description is given of the design and construction of an aluminum block heater, drilled with holes to contain test tubes for the aging of rubber or other organic materials at temperatures up to 800° F.

## ACKNOWLEDGMENT

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[3] Product Packaging Engineering, Culver City, Calif. Comet Model 600 laboratory aging block. Also distributed by C. P. Hall Co., Akron, O.

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